보건학석사 학위논문

Source apportionment of $PM_{2.5}$ using various receptor models in Daebu Island, Korea

수용모델을 통한 대부도 지역 대기 중

$PM_{2.5}$의 오염원 추정

2017 년 8 월

서울대학교 보건대학원

환경보건학과 대기환경전공

김 선 혜

SUMMARY

Source apportionment of $PM_{2.5}$ using various receptor models

Sun-Hye Kim

Department of Environmental Health Sciences

Graduate School of Public Health

Seoul National University

Chemical characteristics of $PM_{2.5}$ play important roles in determining its effect on climate change and human health. Because of its chemical complexity which reflects properties of various environments, characterization of chemical species in $PM_{2.5}$ help trace back where it has been originated. Receptor models have been used as one of source apportioning methods with a chemically speciated data set. As several kinds of literature recommended combining various receptor models to make sure robust source identification results, several receptor model results were discussed with filter-based $PM_{2.5}$ data in this study.

For the source apportionment of $PM_{2.5}$ using Positive Matrix Factorization (PMF) were used. A total of 83 samples were collected from May 21 to November 1 in 2016. The average $PM_{2.5}$ mass concentration was 26.2 ± 14.5 μg m^{-3} with the highest concentration in May (46.5 ± 14.7 μg m^{-3}) and the lowest concentration in August (18.6 ± 8.1 μg m^{-3}). During the sampling period, potassium (K) and sulfate (SO_4^{2-}) showed the highest concentration of trace metals and ion species, respectively. The average OC/EC ratio observed in this study indicated the high possibility of formation in Secondary Organic Aerosols (SOAs) around the sampling site. Carbonaceous compounds in $PM_{2.5}$ was characterized with high water soluble organic carbon to organic carbon ratio (WSOC/OC) in a summer, indicating frequent photo-chemical reactions. For the speciation of individual organic compounds, a total number of 38 samples were gathered through a high-volume air sampler from May 27 to October 30 in 2016. The average sum of individual organic compounds was 116.05 ± 66.19 ng m^{-3}, accounting for 1.97% of the average organic carbon (OC) concentration. Dicarboxylic acids (DCAs) concentration was highest (78.75 ± 57.12 ng m^{-3}) of the average sums followed by n-Alkanoic acids (26.26 ± 9.28 ng m^{-3}), n-Alkanes (10.02 ± 7.46 ng m^{-3}), Sugars (0.54 ± 0.01 ng m^{-3}), and PAHs (0.48 ± 0.42 ng m^{-3}).

In total, nine sources were identified using PMF, which were Secondary Sulfate (29.0%), Mobile (22.0%), Secondary Nitrate (13.2%), Oil combustion (10.1%), Coal combustion (9.4%), Aged Sea Salt (7.9%), Soil (5.6%), Non-ferrous Smelter (1.7%) and Industrial Activities (1.1%). From hybrid receptor models results, high contributions of secondary aerosols from east coastal regions of China was suggested while other expected sources were originated from the industrial complex in inland areas of South Korea or Shandong peninsula in China. The analysis results of organic compounds were added with 38 samples to perform Principal Component Analysis

(PCA). Six factors from PCA were Secondary Organic Aerosols 1, SOAs 1 (38.568%), Combustion related sources (20.170%), Secondary Organic Aerosols 2, SOAs 2 (10.191%), Secondary inorganic factor (7.434%), Biomass burning (5.833%), and Industrial sources (4.455%).

Both of two receptor model results indicated that elevated $PM_{2.5}$ concentrations observed in Daebu Island were mainly attributable to secondary aerosols and combustion sources. Secondary aerosol compounds were mostly from long-range transport from China, whereas combustion sources were from various regions in North Korea, China, and highly contributed in Industrial regions of South Korea.

Tables of Contents

List of Tables

List of Figures

Chapter 1. Introduction

1.1 Background

Fine particulate matter ($PM_{2.5}$) in the atmosphere is a big concern worldwide due to its adverse effects on the human body. Its size characteristics and large surface area per unit mass allow them easily penetrable to the respiratory system causing cardiovascular disease, respiratory irritation and pulmonary dysfunction (Xie et al. 2016).

The chemical composition of $PM_{2.5}$ is a factor affecting health risk and therefore effect estimates could be different from its origins since its chemical characteristics reflect where it has been formed (Bell et al. 2014). Both inorganic element and organic compounds in $PM_{2.5}$ can be utilized as source indicators but most studies done in Korea based on the analysis of inorganic species owing to complex steps in quantifying individual organic compounds. Organic compounds accounting for nearly 20% to 80 % of the total mass of $PM_{2.5}$, composed of over thousands individual organic species (Ackerman et al. 2004). Defining those individual carbonaceous compounds would not only help deepen the understanding of source origins but also help develop environmental health policies with toxicological information. In this study, various instruments were used to quantify different kinds of chemical species in $PM_{2.5}$. Chemical compounds were determined through Inductively Coupled Plasma Mass Spectrometry (ICP-MS), OC/EC aerosol analyzer, Ion Chromatography (IC), and TOC-V analyzer. Besides, individual organic groups were identified with Gas Chromatography-Mass Spectrometry (GC-MS). Overall, the quantification of $PM_{2.5}$ was preceded in each step of the respective chapter using

those different analytical instruments.

Chemical properties of fine particles itself can give the information of its origins but they can be put together into a receptor-oriented or receptor model, estimating the source types and its contributions based on the mass balance techniques (Hopke 2003). Applying a receptor model provides quantified contribution information to each source and therefore enables a government to plan more specific strategies to control air pollutants. Various types of receptor models have been utilized in accordance with situations in previous studies, for instance, the existence of source libraries or the amount of sample data sets can be factors determining which type of models to choose. However, source identification solely based on a certain model might give biased information to a user since each method has a difference in its strengths and drawbacks. Even though several literatures have been highlighted that combining each receptor model is highly recommended to make sure robust source apportionment (Norris et al. 2008), relatively fewer studies have been adopted the combined receptor model method in Korea. This study covers identifying chemical characteristics, source apportionment, and estimating source locations of $PM_{2.5}$ in multiple ways. For a better explanation, various instrumental analyses and receptor model techniques were adopted.

1.2 Research objectives

The main objectives of this study are to

(1) Characterize the inorganic and organic compositions of ambient fine particles ($PM_{2.5}$) with seasonal variations over the sampling period in Daebu Island.

(2) Estimate the source apportionments of $PM_{2.5}$ in the sampling site using two different receptor models: Positive Matrix Factorization (PMF) and Principal Component Analysis (PCA).

(3) Identify the local and long-range transport characteristics of $PM_{2.5}$ applying hybrid receptor models.

(4) Use organic tracer compounds and diagnostic parameters to identify major source types around the sampling area.

1.3 Structure and overview of thesis

In the Chapter 1, the backgrounds and goals of the study are provided with the overview of thesis. The brief outline of Chapter 2 and Chapter 3 is summarized as follows while conclusions of the whole chapter along with recommendations for further research are discussed in Chapter 4.

Chapter 2. Source apportionment of $PM_{2.5}$ using Positive Matrix Factorization (PMF)

Source apportionment through the Positive Matrix Factorization (PMF) method is known to be suitable in Korea where there is a lack of well-developed source libraries. Taking into account the sample size, filter-based $PM_{2.5}$ data set including $PM_{2.5}$ mass concentrations, trace metals, ions, and OC/EC compounds were combined as PMF input data, considering a large amount of data set (>100) is recommended to acquire robust results from the model. The associated PMF results with hybrid receptor models were used to trace back potential $PM_{2.5}$ source areas. This chapter identifies possible $PM_{2.5}$ source factors using PMF receptor models which have been widely used in previous studies. Overall, the study results could be used for monitoring $PM_{2.5}$ sources and identifying $PM_{2.5}$ chemical composition around the sampling site.

Chapter 3. Characteristics of organic compounds and source apportionment using Principal Component Analysis (PCA)

Among organic compounds in $PM_{2.5}$, non-degradable compounds that carry chemical characteristics of their origins are called organic molecular markers or organic fingerprints. These markers are used as effective indicators to distinguish ambiguous sources such as gasoline-diesel mixed sources or combustion related sources. Along with the chemical speciation results from the previous chapter, a total 77 of individual organic compounds were applied to reveal carbonaceous characteristics and assess the source identification. Three source-identification methods, PAHs diagnostic ratio, CPI values, and WNA%, were used to suggest the contributing types of source or aging state of $PM_{2.5}$ associated aerosols. Due to the

relatively small number of data (n=38), Principal Component Analysis (PCA) method was applied to determine possible sources around the sampling site.

References

Ackerman, Andrew S, Michael P Kirkpatrick, David E Stevens, and Owen B Toon. 2004. "The impact of humidity above stratiform clouds on indirect aerosol climate forcing." *Nature* no. 432 (7020):1014-1017.

Bell, Michelle L, Keita Ebisu, Brian P Leaderer, Janneane F Gent, Hyung Joo Lee, Petros Koutrakis, Yun Wang, Francesca Dominici, and Roger D Peng. 2014. "Associations of PM2. 5 Constituents and Sources with Hospital Admissions: Analysis of Four Counties in Connecticut and Massachusetts (USA) for Persons> or= 65 Years of Age." *Environmental Health Perspectives (Online)* no. 122 (2):138.

Hopke, Philip K. 2003. "Recent developments in receptor modeling." *Journal of chemometrics* no. 17 (5):255-265.

Norris, Gary, Ram Vedantham, Katie Wade, Steve Brown, Jeff Prouty, and Chuck Foley. 2008. "EPA positive matrix factorization (PMF) 3.0 fundamentals & user guide." *Prepared for the US Environmental Protection Agency, Washington, DC, by the National Exposure Research Laboratory, Research Triangle Park*.

Xie, Yang, Hancheng Dai, Huijuan Dong, Tatsuya Hanaoka, and Toshihiko Masui. 2016. "Economic impacts from PM2. 5 pollution-related health effects in China: A provincial-Level analysis." *Environmental science & technology* no. 50 (9):4836-4843.

Abstract

Chapter 2. Source apportionment of $PM_{2.5}$ using Positive Matrix Factorization (PMF) in Daebu Island, Korea

Sun-Hye Kim

Department of Environmental Health Sciences

Graduate School of Public Health

Seoul National University

The receptor model defines the possible sources of ambient aerosols based on the observed chemical composition concentration at the sampling site. Daebu Island is geographically located in the west coast of South Korea, showing various regional properties, such as coastal and rural, while it is also close to metropolitan cities and industrial complexes.

From May 21 through November 1 2016, daily filter samples were collected at the rooftop of official residence at Daebu elementary school. To define the pathway and sources of fine particulate matter ($PM_{2.5}$) around this area, Positive Matrix Factorization (PMF) was performed with chemical speciation results from Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Ion Chromatography (IC), and OC/EC aerosol analyzer. A total of 18 trace metal components, organic carbon, elemental carbon, anions, and cations were targeted as well as $PM_{2.5}$ mass concentrations and the results are briefly suggested in this study. Identified PMF results were Secondary Sulfate (29.0%), Mobile (22.0%), Secondary Nitrate (13.2%),

Oil Combustion (10.1%), Aged Sea Salt (7.9%), Soil (5.6%), Non-ferrous Smelter (1.7%), and Industrial Activities (1.1%).

Identification through Conditional Probability Function (CPF) and Potential Source Contribution Function (PSCF) added the explanation of its local sources and long-range sources by combining source apportionment results with meteorological data sets. Large amounts of anthropogenic sources (i.e. Mobile, Coal Combustion, Oil Combustion etc.) were expected to originate from industrialized area: power plants and metropolis. The long-range transport of secondary aerosols indicated that Shandong province and Jiangsu province in China as the principal source areas.

From these study results, the public health strategy for monitoring and regulating $PM_{2.5}$ can be effectively planned based on scientific grounds. As the site is placed between China and the west coast of Korea, transboundary effects around the Island could also explain the regional characteristics.

Keywords: Fine particulate matter ($PM_{2.5}$), Source apportionment, Positive Matrix Factorization (PMF), Conditional Probability Function (CPF), Weighted Potential Source Contribution Function (PSCF)

Student Number: 2015-24104

2.1 Introduction

Fine particulate matter ($PM_{2.5}$), smaller than 2.5 micrometers in diameter are known to have a close relationship with adverse health effects (Stafoggia et al. 2017, Wang et al. 2017). Because of its physical and chemical properties, ambient fine particulate matters can easily penetrate into the human respiratory system and enhance the possibility of pulmonary diseases like lung cancer (Raaschou-Nielsen et al. 2013), asthma, chronical obstructive pulmonary disease, and pulmonary inflammation with oxidative damage on pulmonary cells (Hogg et al. 2004). Cardiovascular diseases might be also triggered by long-term exposure of airborne particulate matters and may possibly enhance the risk of a myocardial infraction (Koton et al. 2013, Madrigano et al. 2013). A report from WHO estimated the societal cost of premature deaths (about 60,000) in 2010 and the total annual economic cost of health impacts, mortality, and morbidity from air pollution to be approximately $1.5 trillion in the WHO European Region (Organization 2015). The critical decrease in visibility by light scattering or light absorbance is another problem that occurs from increasing ambient $PM_{2.5}$, as disturbing the photosynthesis process of crops results in a loss of crop yields (Liu et al. 2014).

As the sources of $PM_{2.5}$ are quite diverse, it is made up of a wide range of chemical components either anthropogenic or natural. Industrial activities, combustions (e.g. fossil fuel, oil, and biomass), cooking, and mobile are defined as the anthropogenic emission sources of $PM_{2.5}$. For example, V and Ni are often used as fingerprints of industrial processes where combustion of fuel oil is proceeded (Viana et al. 2008). In contrary, some airborne particles are formed naturally, for example, volcanoes, living vegetation, forest fires, and sea spray consist of about 90% of atmospheric

aerosols (Taylor 2002). Allergens and microbial particles are also contained in some airborne biological particles and are considered to be very apparent in terms of their effects on health risks (Kim, Kabir, and Kabir 2015). The inorganic components of $PM_{2.5}$ commonly occurs from crustal constituents, such as phosphate (PO_4^{3-}), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), silicon (Si), and aluminum (Al) (Schlesinger 2007). Secondary inorganic components (sulfate SO_4^{2-}, nitrate NO_3^-, and ammonium NH_4^+), organic components, and trace metal components are also generally-found compounds in $PM_{2.5}$ all over the world.

With the growing concerns for the management of fine particulate matters, various receptor models such as Positive Matrix Factorization (PMF) (Paatero and Tapper 1994), Chemical Mass Balance (CMB) (Pace and Watson 1987), Principle Component Analysis (PCA) (Thurston and Spengler 1985), and EPA UNMIX (Henry and Norris 2002) have been developed for the past few decades as effective tools for monitoring air pollution sources. These receptor models identify source contributions based on the principle of mass conservation and mass balance analysis (Hopke 2003) where the ambient chemical mass concentrations data set from receptors are utilized for the mass balance equation.

High concentration of $PM_{2.5}$ due to rapid urbanization and industrialization have been especially the matter of great concern in East Asia (i.e. Korea, China, and Japan) and it is noticeable that the role of East Asia Countries is very important in terms of effective control of global air pollution sources (Wang et al. 2014). With the fast expansion of Chinese economy, extreme haze and $PM_{2.5}$ events not only affect the country itself but lead to long-range transport of aerosols to other countries (Coulibaly et al. 2015, Oh et al. 2015). While the Chinese Government launched a National Plan on Air Pollution Control in 2012 and published various research

outcomes, relatively fewer attentions have been paid to air pollution studies in Korea.

Daebu Island, which is the sampling site in this study, has been affected by various air pollution sources with both anthropogenic (i.e. coal-fired power plants, industrial complex, and traffic) and natural (i.e. sea salts) sources due to its geographical characteristics. In this study, source identification based on PMF model was performed with chemical speciation data for estimating potential sources. For the better understanding of $PM_{2.5}$ source pathway, hybrid receptor models (Conditional Probability Function, CPF and Potential Source Contribution Function, PSCF) were performed using meteorological data set with source contribution results. This study aims the interpretation of potential sources in Daebu Island with PMF model using chemical characterization results.

2.2 Methodology

2.2.1 Sampling site description

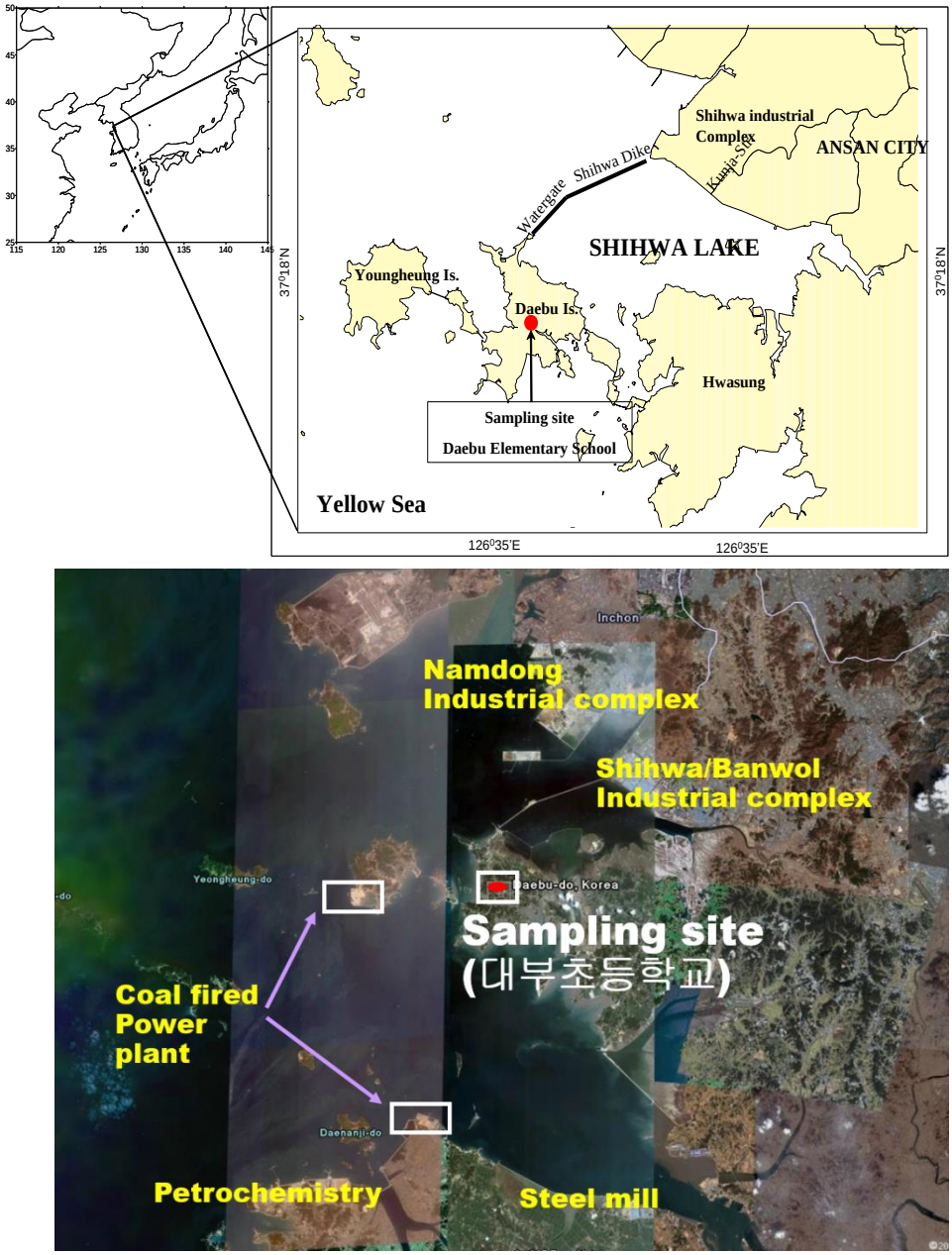

Fig. 2-1. Sampling site (Daebu Island) of this study

Daebu Island (126°35′E, 37°15’N) is a coastal region, which is located 40 km

southwest of the center of Seoul. The total area of the Island is 40.34 km^2. Having the total population of about 7,692 in 2015. The regional characteristics of Daebu Island are relatively complicated, between the megacities and background monitoring site (Deokjeok Island, about 39.4 km west of Daebu Island) of South Korea. The site is also near Yeong-heung coal-fired power plant and Sihwa-Banwol Industrial clusters. Yeong-heung coal-fired power plant is one of main power plants in South Korea and it consists of power station of unit 1 to 6 (Gross capacity :5,080 MW), supporting approximately 25% of the power consumption in Seoul metropolitan area ("Yeongheung Division,"). The Shiwa-Banwol industrial complex, where small to mid-sized industries are located has about a total number of 9,484 companies and 172,000 employees as of 2007. The major type of industries in the Sihwa-Banwol Industrial cluster are machinery, electronics, petrochemicals, and steel in decreasing order (Hyo and Mohan , Kang et al. 2016). The monitoring site is located at Daebu elementary school in the center of Daebu Island (Fig. 2-1). Low volume air samplers were installed on the roof of Daebu elementary school's official residence (126°34'E, 37°14'N, 12 m above ground).

2.2.2 Sampling method

$PM_{2.5}$ samples (n=83) for trace metals, ions, and OC/EC were collected every two days over 24-hr (00:00 – 24:00 UTC+9/KST) from May 21 to November 1 in 2016 through a low volume air sampler (3-channel filter pack system, URG) at the rooftop of building at Daebu elementary school (126°35′E, 37°15'N, rooftop of 12 m). Each filter pack system is connected with size-selective cyclones (URG-2000-30EH, URG) for the selective collection of particles with aerodynamic diameter less than 2.5 μm. Dry gas meter based flow rate for the three channels was 16.7 L min^{-1}, respectively.

Three-channel filter-based samples for each filter pack system and its flow rate within the 10% range of 16.7 L min^{-1} were verified as acceptable data while the flow rates over or below the criteria range were not used in analysis processes.

Teflon filters (PALL science, 47 mm, 1 μm pore size) were used for the calculation of $PM_{2.5}$ mass concentration and collection of trace metals. The mass concentration of Teflon filters was determined gravimetrically by weighing the filters before and after the sampling event using microgram balance (Sartorius, Japan, sensitivity of ± 0.01 mg). $PM_{2.5}$ collected Teflon filters were stored in the thermos-hygrostat (temperature: 20.0 ± 2 °C, relative humidity: 24 ± 5%) for 24 hours before the weighing procedure. The differences between three successive mass concentrations were within the range of 0.03 mg. Lab blank filters were also measured with the sample filters before and after sampling procedure. Lab blank mass values were subtracted from the averaged mass concentration of three-time weighed sample Teflon filter values. The sample filters were then kept in the freezer before the analysis of trace metals.

Quartz fiber filters (Whatman™, 47 mm) were prepared at 450 C° for 12 hours to decrease pre-existing carbon concentration level before the sampling. Quartz fiber filters were used to determine Organic Carbon (OC) and Elemental Carbon (EC) concentrations in $PM_{2.5}$.

Ion compounds of $PM_{2.5}$ were collected on the Zefluor filters (PALL science, 47 mm, 0.1 μm pore size). Before collecting samples, Zefluor filters were soaked with ethanol and rinsed in distilled deionized water (conductivity of 18.2 MΩ cm). Those pre-process were conducted for eliminating possible ion contaminations in the blank filters.

2.2.3 $PM_{2.5}$ chemical speciation analysis

Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Platform ICP, Micomass Inc., UK) were used to analyze trace metals in $PM_{2.5}$ (Cr, Mn, Cu, Fe, Ni, Pb, Cd, Mg, Al, V, Sr, Na, K, As, Se, Ca, Zn, and Co). Teflon filters were soaked with HCl and HNO_3 solvent mixture (1:3) for extraction processes. A closed Microwave Assisted Reaction System (MARS) with 100mL Teflon-lines vessels are utilized to help digestion of sample based on EPA method 3051A. After a pre-digestion process of heating for 20 min, the filter decomposition process was allowed at a temperature of 200 °C for 1 hr. The sample solution was then transferred to the Falcon™ tube for the dilution with deionized water (18.2 MΩ cm). A final dilution volume of 12 mL (5% of original solution) was used for ICP-MS analysis.

Organic Carbon (OC) and Elemental Carbon (EC) concentrations were determined by OC/EC aerosol analyzer (Sunset Laboratory Inc., USA) using the TOT (Thermal-optical-transmittance) method with NIOSH 5040 protocol (NIOSH 1999). During the quantitative procedure, OC is firstly removed during the elevation of temperature (maximum temperature of 870 °C) using helium (He) as a carrier gas. After OC is removed from Quartz fiber filters, oven heaters are turned off for cooling and 2% oxygen mixed in helium gas is injected for the removal of remaining compounds, which is considered as elemental carbon until maximum temperature reaches 870 °C. The absolute quantities of OC and EC are determined by quantifying methane gas (CH_4).

Anions (Cl^-, NO_3^-, and SO_4^{2-}) and Cation (NH_4^+) were speciated using Ion chromatography (IC, Dionex Co., DX-1100, USA). Zeflour filter collected $PM_{2.5}$ samples were extracted in 30 ml of distilled deionized water and then ultrasonicated

for 60 C° for 4 hours. Extracted filter solutions were filtered using syringe filters (PALL science, 0.2 μm pore size) before moving to Ion chromatography auto-sampler vials. The IC analysis was performed by the anion column (Ionpac AS14A 4, 250 mm) and the cation column (Ionpac CS12A 4, 250 mm). Na_2CO_3 with $NaHCO_3$ dissolved in DI water is used as anion eluent and Methane Sulfonic Acid (MSA) solution with DI water is utilized for cation eluent.

The quality control and quality assurance (QA/QC) of $PM_{2.5}$ sample data was proceeded in each analytical steps. The check standard recovery (%) of trace metals was conducted with standard concentration of 10 ppm. The average standard recovery (%) of 7 samples were Cr (97%), Mn (87%), Cu (101%), Ni (105%), Pb (82%), Cd (95%), Fe (142%), Mg (93%), Al (104%), V (84%), Sr (83%), Na (111%), K (111%), As (92%), Se (95%), Ca (172%), Zn (103%), and Co (90%). The filter blank samples are handled in the same procedure of $PM_{2.5}$ sample data and each concentration value was subtracted from originally calculated sample concentration. For the carbon analysis, sucrose standard solution (0.71 g in 100 mL DI water) was checked before starting the sample analysis and every recovery rate of standard solution (5 ml, 10 ml, and 15 ml) should be within the range of ± 5%. Sample reproducibility was identified by measuring duplicates of sampled filters in every 10 sample and acceptable criteria range was ± 10%. In the case of ion species, 1ppm of check standard was measured every 10 sample where the acceptable recovery range was 80% to 120%. The R^2 value of each standard calibration curve was ranged from 0.98 to 0.99.

2.2.4 Receptor model analysis

2.2.4.1 Positive Matrix Factorization (PMF)

The Positive Matrix Factorization (PMF) model, which is a progressed factor analysis in terms of providing non-negative source profiles, originally developed from Paatero (Paatero and Tapper 1994) as an alternative to conventional factor analysis model. PMF has its strong points in dealing with error estimates of practical environmental data compared to other former receptor models like Factor Analysis (FA) or Principal Component Analysis (PCA).

The main objective of PMF is to minimize function Q (1) and the solution is provided by calculating G and F values in iterative minimization algorithm (PMF2).

$$Q(E) = \sum_{i=1}^{m} \sum_{i=1}^{n} \left[\frac{e_{ij}}{s_{ij}}\right]^2 \quad (1)$$

In this equation, e_{ij} is called residual element where i is 1,…, n elements, j is 1,…, m samples, k is 1,…, p sources and x_{ij} is the standard deviations for each data point. s_{ij}, uncertainty estimates in the ith elements of jth samples measured is known value from the user and it is used to calculate minimum Q value.

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} f_{ik} g_{ik} \quad (2)$$

Further description in detail is well explained in several other studies (Paatero 1997, Paatero and Tapper 1994) and EPA PMF 5.0 User Guide (Norris et al. 2014).

A large number of fine particulate matter sample data is necessary to solve the mass balance equation and identify proper source profiles. Even though the number of samples in this study is a little bit under one hundred (n=80, three of samples were

not used for modeling), the application of PMF is still effective for identifying possible sources whereas the source profiles are unknown. The PMF model is especially suitable in Korea where specific source profile libraries have not been created yet (Heo, Hopke, and Yi 2009). Study examples of applying PMF model at monitoring sites in Korea can be found in other papers (Han et al. 2005, 2006, Moon et al. 2006, Moon et al. 2008, Heo, Hopke, and Yi 2009, Oh, Lee, and Kim 2009, Lim et al. 2010b, Oh, Lee, and Kim 2011, Choi et al. 2012, 2013, Yi and Hwang 2014, Jeong and Hwang 2015, Lee et al. 2015, Oh et al. 2015).

In this study, PMF (EPA PMF version 5.0) was used for the source apportionment of $PM_{2.5}$. For the missing values, arithmetic mean concentration of the chemical concentration was used as a replacement. Concentration values that are less than zero or equal to zero were change to 1/2 of methods detection limits (MDL) of the each element. For the uncertainty of sample data which is below or equal to zero, 5/6 of MDL values were applied to replace the original values. Missing concentration values and uncertainty values were replaced by the geometric mean of the element and 4 times the geometric mean respectively. The F_{PEAK} value of PMF was adjusted to 0 after several adjustments trials from -1 to 0.

2.2.4.2 Hybrid methods

Conditional Probability Function (CPF)

Conditional Probability Function (CPF) was applied in this study to estimate local scale point source effects with wind direction data from the receptor. CPF is very effective tool for showing the dominant wind directions of potential source areas. The equation (3) below explains the basic principle of CPF.

$$\text{CPF} = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \quad (3)$$

where $m_{\Delta\theta}$ is the number of times that source contribution greater than threshold criteria that passed the given sector $\Delta\theta$. $n_{\Delta\theta}$ is the number of occurrences that passed the sector $\Delta\theta$ at the same time. The 75th percentile of calculated fractional source contribution value was used as the threshold criteria and sector ($\Delta\theta$=22.5°) was applied for the CPF. R software (version 3.2.1) package was used for showing polarPlot of identified sources based on the CPF function in this study. The polar CPF plots provide additional information of wind speed, which is helpful to interpret source contribution results.

The meteorological data from the receptor site were obtained from the website of Korea Meteorological Administration (KMA). Each of daily fractional source contribution data from PMF model was combined with the hourly meteorological data to calculate CPF values. Associated daily values for the source contribution were applied to each hourly data of the same day.

Potential Source Contribution Function (PSCF)

While the CPF model is effective to infer the source direction of local sources, it has limitations to implementation for long range transport. The Potential Source Contribution Function (PSCF) model (Ashbaugh, Malm, and Sadeh 1985) has been widely used to identify potential source areas of long-range transport. The model represents the conditional probability of an air parcel which passed the area over certain high concentration level and the equation is represented below equation (4).

$$PSCF = \frac{m_{ij}}{n_{ij}} \quad (4)$$

where n_{ij} represents the total number of trajectory endpoints that passed ij th grid cell. m_{ij} represents the total number of times where the trajectory endpoints high enough to exceeded the threshold concentration level in the same grid. The criteria value of m_{ij} in this study was assigned to 75th percentile. PSCF is a hybrid model which combines the backward trajectory results obtained from NOAA HYSPLIT 4 model (HYbrid Single Particle Lagrangian Integrated Trajectory, NOAA's Air Resources Laboratory, 2009) with the daily fractional source contribution results from PMF. For the backward trajectory modeling, Global Data Assimilation System (GDAS) data resolution of $0.5° \times 0.5°$ was used as a meteorological input data. Back trajectory hours, traced back 96 hours (four-day back) and starting height in this study were set to the half of mixing height above ground level. For reducing the effects of uncertainties with small n_{ij} value, the weight function W (n_{ij}) was applied as shown below in equation (5).

$$W(n_{ij}) = \begin{cases} 1.0, & (n > 3n_{\text{avg}}) \\ 0.8, & (2n_{\text{avg}} < n \leq 3n_{\text{avg}}) \\ 0.6, & (n_{\text{avg}} < n \leq 2n_{\text{avg}}) \\ 0.4, & (0.5n_{\text{avg}} < n \leq n_{\text{avg}}) \\ 0.2, & (n \leq 0.5n_{\text{avg}}) \end{cases} \quad (5)$$

The result of weighted PSCF images were obtained using geographic information system (GIS) based program (ArcMap^{TM}10 software).

2.3 Results and discussions

2.3.1 Chemical speciation results

The overall $PM_{2.5}$ mass concentration trends during May 21 to November 1 in 2016 were described in the supplementary Fig. S2-1. Among 83 samples, a total of 80 sample data, except three samples which contain flow errors, were analyzed for the receptor modeling. The average concentration during the sampling period was 26.2 ± 14.5 μg m^{-3}. The average concentration in this study exceeded the annual average $PM_{2.5}$ criteria concentration (15 μg m^{-3}) of US EPA. The result showed that 59 of the total samples (73.75%) exceeded the US EPA criteria. Meanwhile, the annual air quality standard of $PM_{2.5}$ in Korea is 25 μg m^{-3} and 38 of the total sample, which is the 47.5% of the total sample were over the criteria. However, the average annual concentration of $PM_{2.5}$ was generally much lower than Seoul, the capital of South Korea (Kang, Kang, and Lee 2006, Heo, Hopke, and Yi 2009)

The monthly trend of $PM_{2.5}$ mass concentration was highest in May (46.5 ± 14.7 μg m^{-3}) and lowest in August (18.6 ± 8.1 μg m^{-3}), which is the late spring and midsummer season in Korea respectively. Except for the average concentration of May which contains relatively less number of samples (n=6) due to the sampling period, June shows the highest concentration (31.3 ± 13.5 μg m^{-3}). It is widely known that PM mass concentrations are higher during the winter and spring than the summer and fall seasons in Korea (Kim, Kim, and Lee 1997). This phenomenon is mainly observed in certain seasons due to Asian Dust (AD) which occurs periodically in the region of East Asia and Pacific from the desert area of China and Mongolia (Kim and Kim 2003). The average mass concentrations of Saturday (24.6

± 15.8 μg m^{-3}) and Sunday (22.8 ± 13.2 μg m^{-3}) were slightly lower than average annual concentrations. The highest concentration during a weekday was revealed as 33.5 ± 16.4 μg m^{-3} on Friday.

A total of 19 metal components (Cr, Mn, Cu, Ni, Pb, Cd, Fe, Mg, Al, V, Sr, Na, K, As, Se, Ca, Zn, and Co) were analyzed with the $PM_{2.5}$ filter-based samples. The monthly trend of trace metals showed similar concentration trends with the monthly $PM_{2.5}$ mass concentration except for Zn, Na, Cu, V, Ni, As and Cr. For the case of Na concentration, it showed the highest concentration in July (0.19 ± 0.17 μg m^{-3}) while most of the trace metals showed the lowest concentrations in July. The trace metal species with the highest average-concentration during the monitoring period was K (0.21 μg m^{-3}).

Among 4 ion species (NO_3^-, SO_4^{2-}, Cl^-, and NH_4^+), the average concentration was highest in SO_4^{2-} (6.14 ± 4.52 μg m^{-3}) while lowest in Cl^- (0.26 ± 0.30 μg m^{-3}). The monthly average concentrations of both anions and cations were highest in May along with the average mass concentration trends. Unlike other three ion species, SO_4^{2-} showed the second highest concentration in August (7.05 ± 3.58 μg m^{-3}). Several studies have been suggested that the concentration of secondary sulfate is generally high during the summer season due to photo-chemical reactions.

The average Organic Carbon (OC) and Elemental Carbon (EC) concentrations were 5.94 ± 3.53 μg m^{-3} and 0.61 ± 0.29 μg m^{-3} respectively. The average annual OC and EC concentrations of Seoul, the capital of South Korea in 2015 were 5.58 μg m^{-3} and 0.92 μg m^{-3} respectively and the average $PM_{2.5}$ mass concentration in the same year was observed as 35.5 μg m^{-3}. Average OC/EC ratios range from 4.0 to 36.9. The

highest monthly OC/EC ratios were 15.78 in May while lowest OC/EC ratios were 7.31 in October in this study.

Both OC and EC concentrations were highest in May and the similar trend of the high concentration during winter period is expected under this concentration trend. The average OC/EC concentration during the sampling period was 10.14. It was widely accepted that OC/EC ratios exceeding 2.0 indicate the presence of Secondary Organic Aerosols (SOAs) (Park, Kim, and Fung 2001). The ambient OC/EC ratios and OC concentrations increase with the formation of Secondary Organic Aerosols (SOAs) and the OC/EC ratios over the expected primary emission ratio indicates the formation of SOAs (Cabada et al. 2004). The emitted OC easily becomes SOAs by chemical reactions in the atmosphere while EC is known as the byproduct of incomplete combustion of OC (Chu 2005).

Table 2-1. Summary of $PM_{2.5}$ species concentration collected in Daebu Island, Korea during the whole sampling period (5/21/2016 to 11/1/2016)

Species	Min ($ng\ m^{-3}$)	25th ($ng\ m^{-3}$)	Median ($ng\ m^{-3}$)	Arithmetic mean ($ng\ m^{-3}$)	75th ($ng\ m^{-3}$)	Maximum ($ng\ m^{-3}$)
$PM_{2.5}$	6418.721	14927.049	22377.550	26205.148	35724.985	65768.465
OC	1503.538	3264.401	5069.678	5903.392	7069.832	21104.491
EC	180.008	405.987	550.189	612.408	735.830	1674.022
NO_3^-	3.752	626.971	1627.378	3062.160	3789.794	15722.082
SO_4^{2-}	94.384	2352.038	5803.736	6141.238	8725.277	17029.499
NH_4^+	1.825	337.875	1778.650	2492.837	4155.158	10098.554
Cl^-	0.545	5.228	79.323	262.591	590.783	1040.002
Cr	0.096	0.096	0.096	0.525	0.096	12.380
Mn	0.114	4.481	7.981	9.589	14.233	39.697
Cu	0.207	2.941	8.873	20.900	18.030	242.746
Ni	0.138	0.138	0.138	4.129	2.841	160.880
Pb	0.464	7.309	15.391	18.265	24.567	89.305
Cd	0.016	0.365	0.649	0.880	1.146	10.561
Fe	3.089	66.910	126.192	160.762	252.453	544.627
Mg	1.272	27.616	38.154	44.247	57.792	133.615
Al	0.157	56.074	93.589	115.277	168.278	346.567
V	0.074	5.197	11.410	12.030	16.637	39.138
Sr	0.015	0.358	0.672	0.767	1.001	2.586
Na	4.090	96.037	144.347	176.022	220.087	602.967
K	5.322	91.618	165.710	214.915	290.023	876.063
As	0.046	1.126	2.776	3.377	5.080	14.742
Se	0.003	0.003	0.003	0.483	0.409	4.044
Ca	0.893	14.804	35.547	54.379	70.928	323.955
Zn	0.355	21.985	55.221	134.471	124.455	2952.174
Co	0.000	0.001	0.044	0.118	0.095	3.575

3.2 Receptor model results

3.2.1 Source apportionment by PMF

Total 80 samples with $PM_{2.5}$ mass concentrations, trace metals, ions, and OC/EC data set were involved in the PMF receptor modeling. Nine factors of source have been identified which are Secondary Sulfate (29.0%), Mobile (22.0%), Secondary Nitrate (13.2%), Oil Combustion (10.1%), Coal Combustion (9.4%), Aged Sea Salt (7.9%), Soil (5.6%), Non-ferrous Smelter (1.7%), and Industrial Activities (1.1%). The confidence of PMF results was identified with linear regression analysis. The R^2 value between observed $PM_{2.5}$ concentration and reconstructed $PM_{2.5}$ concentration was described in Fig.2-2 as a concentration scatter plot. The axis of x represent the sum of resolved source contribution results from the PMF whereas the y axis explain the observed $PM_{2.5}$ data from the experiment. The R^2 value of 0.83 represented a general good agreement with correlations between two variables.

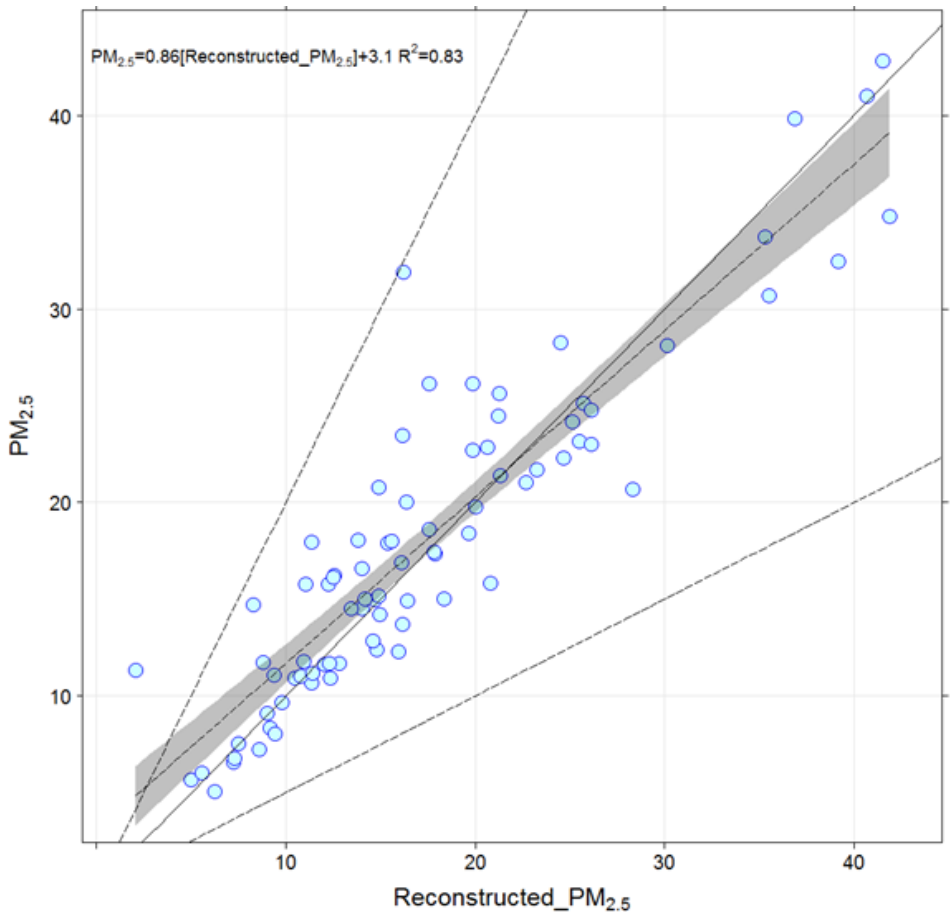

Fig. 2-2. Concentration scatter plots of PMF. Correlation between predicted (reconstructed) concentration value using PMF and measured concentration value using linear regression method explains an R^2 value of 0.83 with the regression slope of 0.86.

Monthly source contribution results of nine sources and the comparison with weekday and weekend contributions were computed (Fig. 2-3). The first dominant factor which accounted for 29.0% of the $PM_{2.5}$ mass concentration was the Secondary Sulfate factor. The Secondary Sulfate factor was identified by the high concentrations of SO_4^{2-} and NH_4^+. It is widely documented that the most common

form of secondary sulfates comes from the neutralization of sulfuric acid by ammonia (e.g. $(NH_4)_2SO_4$) (Biggins and Harrison 1979) and this fact supported the apportionment result from the study result. Secondary sulfate is formed by the reaction of primary sulfate with other chemical compounds and the reaction can be speeded up in the summer. From the monthly source distribution result, higher concentration of secondary sulfate in summer season (June-August) was identified and this elevation trend already has been discussed in other former researches (Cohen, Martin, and Bailey 1993, Chow et al. 1994, Chan et al. 1999), which explained the reason as much more chances of homogeneous reaction with OH radicals in summer. The sulfur is often emitted as a form of secondary sulfate originating from SO_2 emissions such as automobiles, coal-fired power plants, and industries (Cohen et al. 2010). It is highly probable that this factor is affected by combustion of coal since the first factor also showed relatively high concentration in Selenium (Se) accompanied by high concentration of Sulfate (SO_4^{2-}). While the sulfate (SO_4^{2-}) is produced by oxidation reaction of SO_2 in the atmosphere, Selenium (Se) generally showed positive relationships with primary source from coal combustions (Lee et al. 2003, Pekney et al. 2006). The formation of secondary sulfate is facilitated from photochemical reactions, for example, the frequent photochemical reactions generally accelerated by stronger solar radiation and hence the reaction causes the elevation of OH radical concentration in the atmosphere. This mechanism may explain the high contribution of secondary sulfate factor during the summer season.

The Secondary Nitrate factor explains 13.2% of the $PM_{2.5}$ mass concentration. NO_3^- was the most dominant species in this factor with a prominent NH_4^+ concentration. Unlike the seasonal distribution of secondary sulfate factor, the second factor showed the elevation trend in non-summer seasons, accounting for the highest percent in May (21.33%) followed by October (18.78%). This contribution trend well agreed

with other study results of ambient fine particulate matters. The seasonal variation of secondary nitrate often peaks during the winter time due to the low temperature and relatively high humidity, which help chemical reactions to form ammonium nitrate (NH_4NO_3) (Alexis et al. 2005). Secondary nitrate concentration was slightly higher in weekends (12.42%) than weekdays (15.16%). The vehicle is also the substantial contributor of nitrates as forms of ammonium nitrate or organic nitrates (Liu et al. 2016). When considering the characteristics of Daebu Island as a tourist attraction, a huge influx of visitors with vehicles were expected and this could possibly affects the elevation of secondary nitrate contribution during weekends. However, the difference of mobile source contribution was not significantly stand out between weekday (22.22%) and weekend (21.40%) concentrations.

The Mobile factor was identified by the high concentration of OC, EC, and Mn. The total source contribution of Mobile factor was 22.0%. Generally, mobile sources have higher levels of EC and OC concentration compared to other $PM_{2.5}$ sources (Louie et al. 2005). The outstanding increase in autumn season (September: 44.43% and October: 34.82%) was discovered rather than other 8 factors. The high contribution of mobile factor during the autumn can be well explained by the mechanism that lower temperature accelerates condensation of vehicle exhaust to form small particles (Mulawa et al. 1997, Charron and Harrison 2003) and previous source apportionment study done in industrial complexes in Korea also showed the highest contribution during the winter (Lim et al. 2010b). The nucleation rate of particles is known to facilitated by higher relative humidity and lower temperature (Shi and Harrison 1999) and it appeared that the meteorological environment in September meet those conditions (Fig. S2-2). There was not large difference in the level of relative humidity between August (86.2%) and September (85.1%) however the average temperature was rapidly decreased from 25.8 ℃ to 21.9 ℃. Particles

that are not firstly exists in the emission gas can be slowly condensed while the road temperature was cooling down and this phenomenon might be mainly occurred in September and October. Monsoons generally blow from the land to the sea during the winter as the temperature in the land rapidly decreases. The CPF result of mobile source (Fig. 2-8) indicated that the mobile source was affected by inland areas near the sampling site. From the regional characteristics, mobile sources can be transported as the monsoons bring the air particles toward Daebu Island.

In the Coal Combustion factor, As, Pb, K, and Cd showed the high concentration while the contribution of the coal combustion to total $PM_{2.5}$ accounted for 9.4%. Cd occurs during the high temperatures of combustion processes like coal combustion, oil combustion, and refuses (Uberol and Shadman 1991). It was also suggested that As and Se as the markers of coal combustion sources (Harrison, Smith, and Luhana 1996). The contribution of Coal Combustion showed the highest concentration in October (2.90 $\mu g/m^3$) in this study. The relatively high concentration in October can be explained by the increase in heating and inversion of air temperature. The prior airborne metal study in Sihwa and Banwol Industrial Complex also supports this trend near Daebu Island with high metal concentrations in fall or spring (Lim et al. 2010a). As discussed before in this study, Secondary Sulfate factor is indicative of the contribution of coal combustions and it showed relatively high contributions in October, which agrees reasonably well with the contribution result of Coal Combustion factor.

The fifth factor, which contains the major indicators of Oil Combustion (V and Ni) contributed 10.1% of the total $PM_{2.5}$ mass. V and Ni are often act as the good indicators of ambient particles emitted from fuel or oil combustion sources (Manoli, Voutsa, and Samara 2002, Almeida et al. 2006).

The Non-ferrous smelter showed the significant concentrations of Cu. Cu, Zn, and Pb are used to be interpreted as the markers for non-ferrous smelter (Swietlicki et al. 1996). 1.7% of the total $PM_{2.5}$ mass concentration attributed to the factor of Non-ferrous smelter. Though the contribution level is not significant in the overall source contributions, toxic metal compounds from non-ferrous smelters and its refining processes may hazardous to health of humans and even animals (Ades and Kazantzis 1988, Fischer et al. 2003, Liu 2003, Yu et al. 2006).

The factor of Industrial Activities which contributed 1.1% of the total $PM_{2.5}$ was characterized by Zn, Ca, V, and Cu. Industrial sources have various kinds of elements since those processes include the use of fossil fuels and mechanical abrasions. V usually comes from the heavy oil combustions (Samara et al. 2003). Both of Oil Combustion factor and Industrial Activities factor involved the lowest concentration in October. Those two factors included anthropogenic activities and the abrupt drop in the October, which seemed to have positive relationships with the activity of industrial plants near the sampling site.

The Soil factor shows high concentration in Ca, Sr, Al, Mg, Fe, Ce, K, and Na. The contribution of soil factor was 5.6%. Several studies indicate that Al, Si, Ca, Fe, Ti, Mg, K, and Na were the most abundant crustal elements of Earth and they were easily found in re-suspended dust or soil sources (Sun et al. 2004). May (7.54%) was the second highest month after October (12.18%) of this factor. The relatively low contribution of soil can be influenced by the frequent rain-wash effect during summer season while Asian Dust (AD) event in May might contribute to its high contribution. The negative correlation between soil and rain factor (Fig. S2-3) and the highest rainfall (mm) in July (Fig. S2-2) during the sampling month support the hypothesis of rain-wash effect during the sampling period. A total of 5 elements

(PM_{10}, SO_2, NO_2, O_3 and CO) and meteorological data set (temperature, wind direction, wind speed, and precipitation) from an air pollution monitoring site in Daebu Island were combined for the correlation analysis using R (version 3.2.1) and the result is shown in supplementary Fig. S2-3.

The Aged Sea Salt factor accounted for the smallest portion (7.9%) of the total $PM_{2.5}$ mass concentrations. The PMF source contribution result of the Aged Sea Salt factor is characterized by high concentration of Na, Mg, and K while the Cl was excluded in the modeling process. The sampling site is surrounded by the west sea of South Korea and it is expected that the most of the Aged Sea Salt factor came from those regional environments. Aged Sea Salt particles typically comprise of S and Cl. The fresh Sea Salt which is known as NaCl transformed into Na_2SO_4, influenced by SO_2 in the atmosphere. High level of S in the marine environment is expected around the sampling site in which the high contribution of anthropogenic sources can be suggested (Sun et al. 2004).

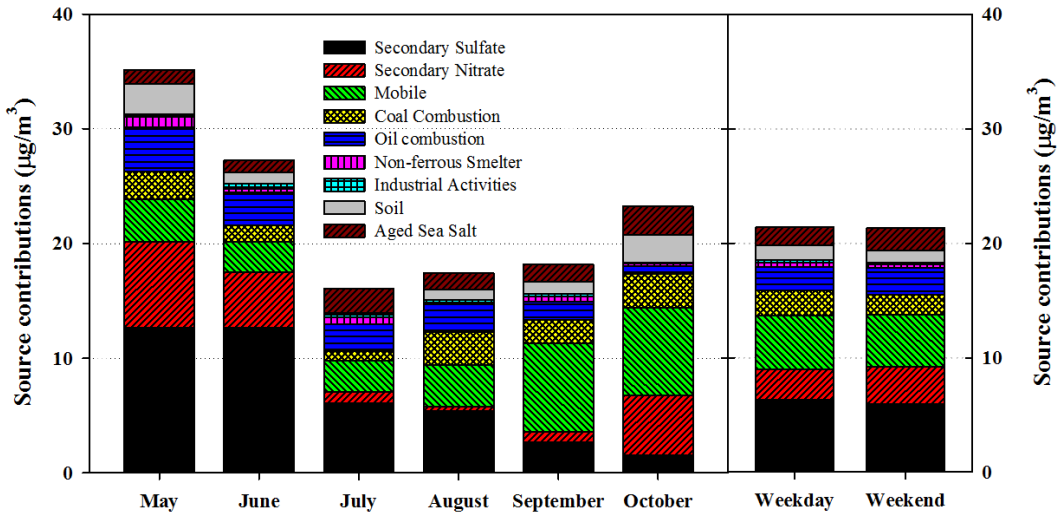

Fig. 2-3. Monthly source distributions (right) and the comparison of weekday with weekend source distributions (left) from PMF results

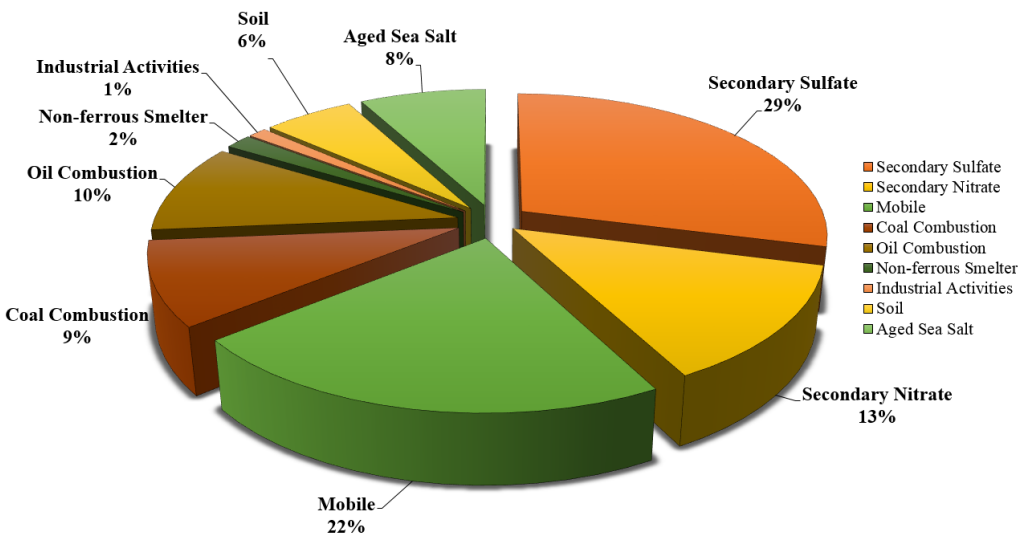

Fig. 2-4. Nine sources of PMF source apportionment result.

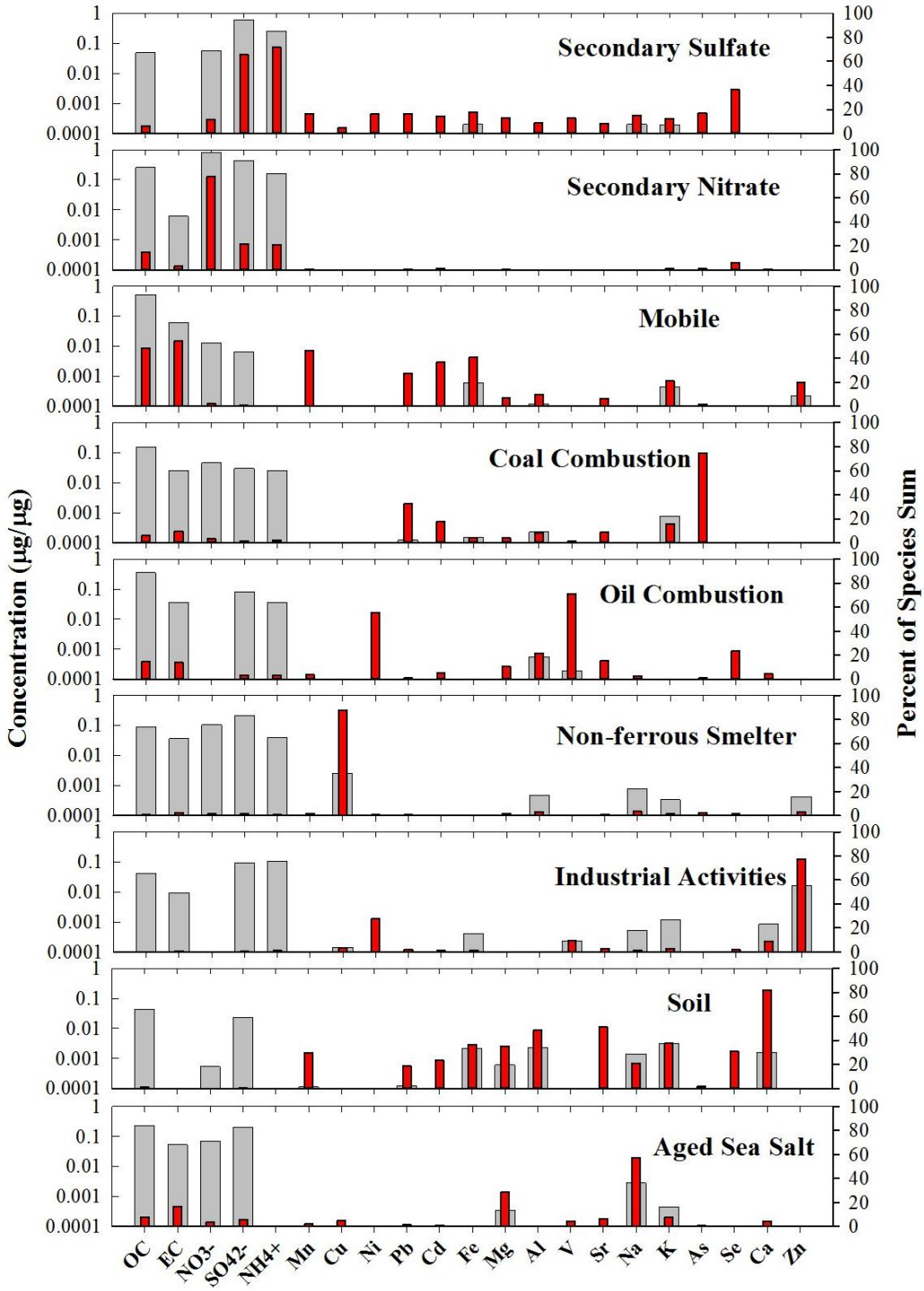

Fig. 2-5. Source contribution plot of $PM_{2.5}$ in Daebu Island, Korea. Source concentration of species (μg/μg) are shown as gray bars in right y-axis (logarithmic scale) while red bars in the left y-axis represent the percent of species

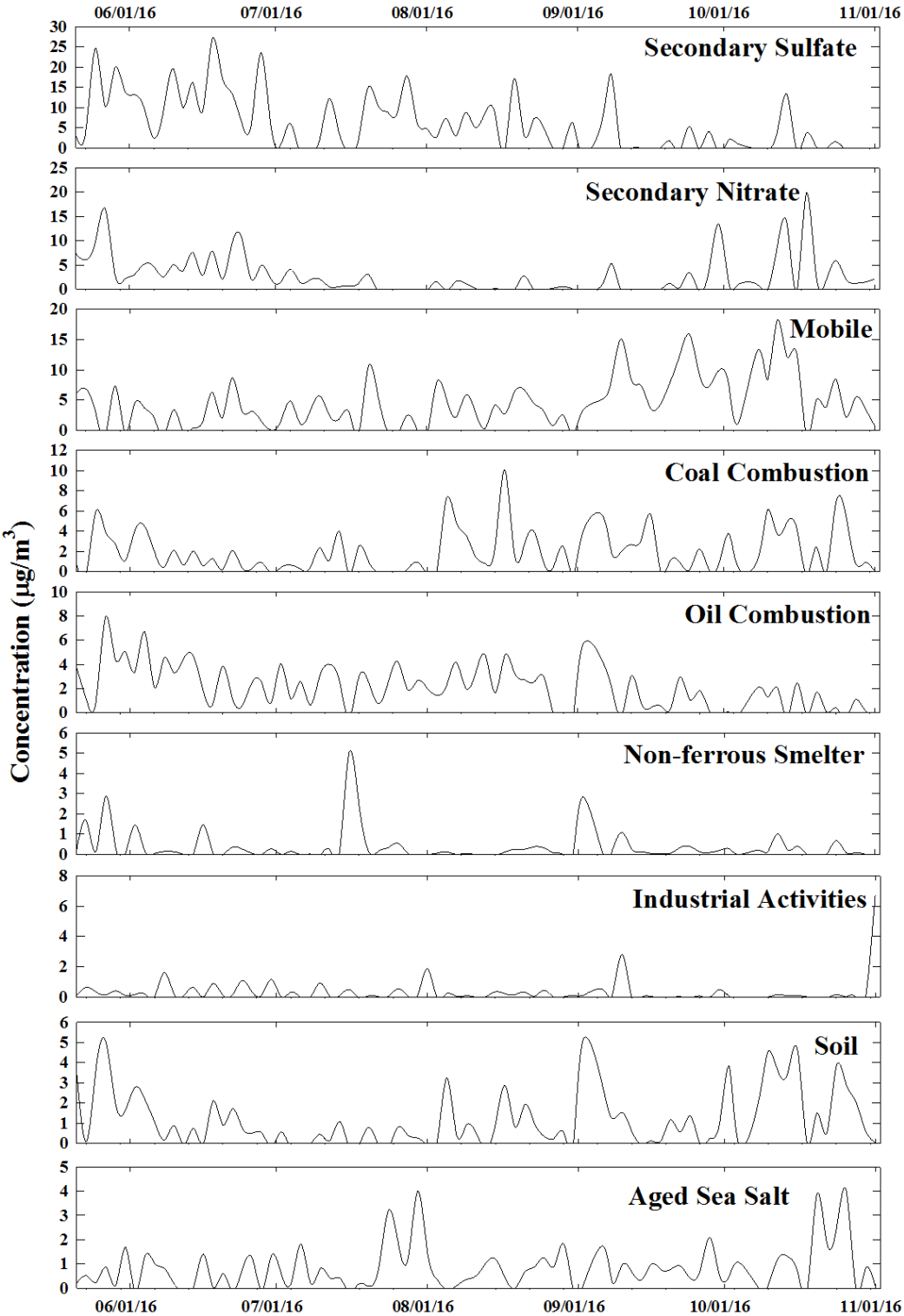

Fig. 2-6. $PM_{2.5}$ source distributions by time series plot in Daebu Island, Korea

Table 2-2. Monthly source contributions (%) of $PM_{2.5}$ in Daebu Island

Sources	Months (aveage ± standard deviation, %)					
	June (n=15)	July (n=15)	August (n=15)	September (n=14)	October (n=14)	Average (n=80)
Secondary Sulfate	46.39 ± 24.99	37.73 ± 36.33	30.77 ± 25.74	14.71 ± 27.98	6.72 ± 15.52	29.00 ± 32.37
Secondary Nitrate	17.98 ± 9.88	6.19 ± 8.35	2.34 ± 5.21	5.05 ± 10.06	22.17 ± 26.38	13.21 ± 19.01
Mobile	9.69 ± 9.09	16.87 ± 18.24	20.87 ± 13.88	42.29 ± 24.48	33.11 ± 22.09	21.99 ± 19.70
Coal combustion	5.25 ± 4.92	5.29 ± 7.50	16.21 ± 15.83	11.41 ± 10.38	12.50±10.20	9.45 ± 10.01
Oil combustion	10.57 ± 6.25	14.66 ± 8.08	14.45 ± 8.12	8.79 ± 9.54	3.01 ± 4.38	10.06 ± 8.38
Non-ferrous Smelters	1.02 ± 1.73	3.71 ± 8.30	0.48 ± 0.76	2.17 ± 3.99	0.97 ± 1.22	1.65 ± 3.69
Industrial Activities	1.67 ± 1.77	1.12 ± 1.65	1.44 ± 2.63	1.44 ± 3.99	0.29 ± 0.58	1.15 ± 2.15
Soil	3.45 ± 3.16	1.41 ± 2.67	5.14 ± 5.71	5.84 ± 7.58	10.41 ± 6.85	5.63 ± 6.55
Aged Sea Salt	4.03 ± 4.41	13.02 ± 14.55	8.29 ± 6.21	8.29 ± 6.39	10.81 ± 11.32	7.88 ± 8.49

Note: Speciation data set of May 21 to 31 and November 1 were included in the average concentration of each source

2.3.2.2 Hybrid receptor model results

Conditional Probability Function (CPF) and Potential Source Contribution Function (PSCF)

The nine source contribution factors from PMF result were combined with the hourly wind data set from Korea Meteorological Administration (KMA). CPF models assist in identifying likely local pollution sources and direction of inflows. To determine the overall wind directions and wind speed of the monitoring site, meteorological data from the roof of the building at Daebu elementary school (126°58'E, 37°25'N) was used. Wind rose plots of the monitoring site during the observation period and the past nine year are suggested in Fig. 2-7 to show the main direction of wind. The wind rose diagrams were plotted in R software (version 3.2.1).

The dominant wind direction in the sampling period (May 21 to Nov. 1, 2016) was primarily from the northwest (NW). The southeast (SE) was the second dominant wind direction while the main wind direction of the past few years also indicated NW and SE as the main direction of wind that have affected the inflow of air parcel.

Secondary aerosols are formed in the atmosphere with the various sources of gas phase chemicals (e.g. sulfur dioxide, nitrogen dioxide and ammonia etc.) and ambient fine particles (Hallquist et al. 2009). It can be explained that both Secondary Sulfate (Fig. 2-8 (a)) and Secondary Nitrate factor (Fig. 2-8 (b)) were mainly affected by southeasterly (SE) and northwesterly (NW). Fig. 2-1 provided probable source information as well as the sampling site description. The sources of Yeong-heung coal-fired power plant and petro-chemistry are likely to show an agreement with the probable direction suggested from CPF plots of secondary aerosols.

The CPF plot of Mobile source factor (Fig. 2-8 (c)) and Coal Combustion factor (Fig.

2-8 (d)) indicated that the high probability of source contribution in Northern (N) areas near the sampling site. There are several industrial complexes such as Namdong and Shiwa-Banwol industrial complexes to the north of the Daebu sampling site. The most abundant compounds in Coal Combustion factor from PMF were Arsenic (As), Lead (Pb), and Cadmium (Cd), which are known to have the high health risk accumulated in human body. The previous study reported that cadmium concentration in PM_{10} showed average concentration of 6.3 ng/m^3 in Banwol industrial complex and 7.1 ng/m^3 in Sihwa industrial complex (Lim et al. 2010a). This concentration level is not only much higher than the air quality guideline from World Health Organization (WHO), where the cadmium criteria level of 5 ng/m^3 (Organization 2000) but the concentration level of the case studies in Pohang, Korea (1.95 ng/m^3) (Kim and Jo 2006), Jeju, Korea (0.47 ng/m^3) (Kim et al. 2006), Northern Europe (0.05-0.2 ng/m^3), Central Europe (0.2-0.0.5 ng/m^3), and Southern Europe (0.06-0.12 ng/m^3) (Aas and Breivik 2005). This results may also indicate those industrial complexes are the main source of coal combustions.

The Mobile factor (Fig. 2-8 (c)) indicated a high probability of being located at inland areas near megacities (Incheon) and industrial cities (Ansan). Since Daebu Island is surrounded by East Sea except the direction of the North (N) and West (W), the majority of the mobile source is expected to originate from big cities near the sampling site.

The Soil factor (Fig. 2-8 (h)) is also distributed in the northeast (NE) areas. This could also be partly from those industrial complexes and China but the PSCF with Concentration Weighted Trajectory (CWT) indicated that soil sources were transported from the North China where frequent dust storm events occur. The northern China including Shandong province has been influenced by a rapid rate of

anthropogenic activities like soil cultivation, overstocking, and overgrazing while fuelwood collection which are responsible for 85% of the degraded soils in the total area (Wang et al. 2006). The sampling site in this study is also close to Deokjeok Island (126°9′E, 37°13’N), where the background monitoring site is located at the western coast of Korea and it is 330 km away from the Shandong region. In the previous study at the two background monitoring sites (Deokjeok and Gosan) in Korea discovered that merely 40% of elevation in secondary aerosols was observed mainly due to long-range transport from eastern China with westerly in the source areas (Kim et al. 2009).

Unlike those sources, Oil Combustion (Fig. 2-8 (e)) source showed high probability in southwesterly (SW) where the location is almost coincide with industrial regions. Industrial complexes such as coal-fired power plant, petrochemicals, and steel industry are popular in Seosan (126°37’E, 36°99’N) and Dangin (126°51’E, 37°09’N) which are about 52 km and 40 km from Daebu elementary school, respectively. The dominant wind direction for both Non-ferrous Smelter and Industrial Activities was southeasterly (SE).

Aged Sea Salt factor (Fig. 2-8 (i)) was greatly influenced by southwesterly (SW), which reflects the direction of yellow sea and chemical industries while the east part of Daebu Island is close to the inland regions of Korean peninsula. As previously discussed, the CPF results also support that the fresh sea salts from the ocean might have been reacted with the anthropogenic sulfur in the atmosphere.

The origin of Non-ferrous Smelter (Fig. 2-8 (f)) and Industrial Activities (Fig. 2-8 (g)) seem to be very similar with south easterly, indicating the direction of multiple industrial complexes in Hwaseong, Gyeonggi-do.

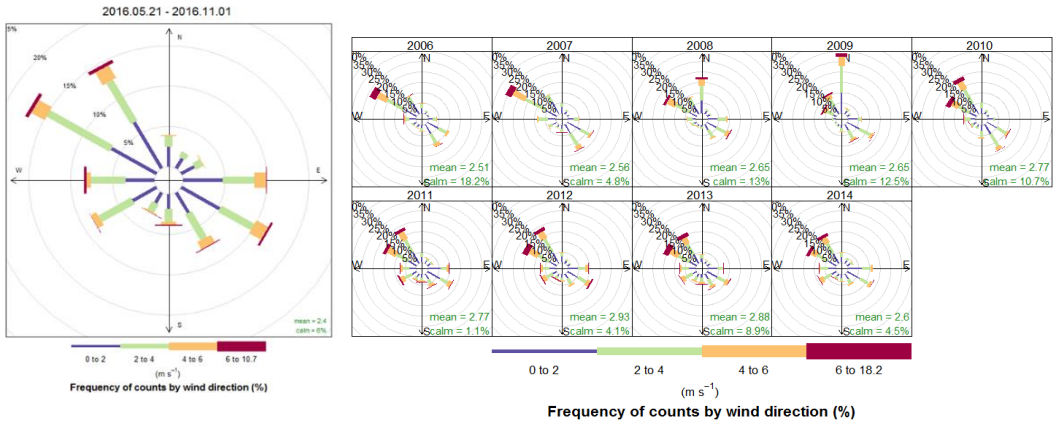

Fig. 2-7. The wind rose plot of the sampling year (left) and wind rose plots of the past nine years (2006 to 2014) (right)

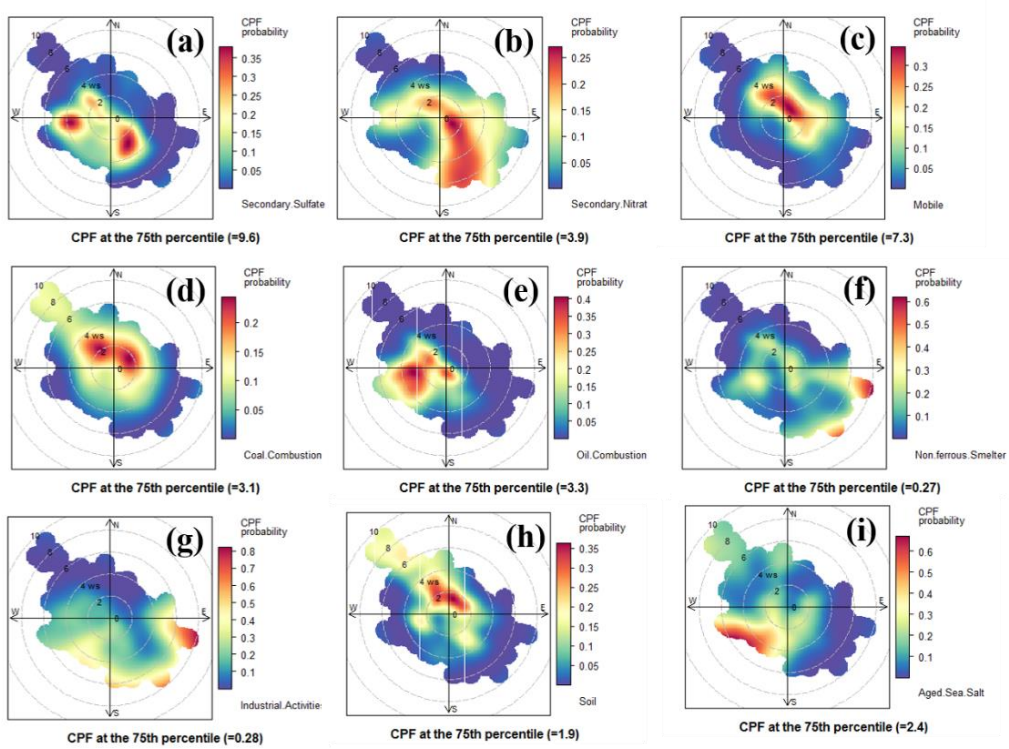

Fig. 2-8. CPF plots of nine sources using PMF in Daebu Island. (a) Secondary Sulfate, (b) Secondary Nitrate, (c) Mobile, (d) Coal Combustion, (e) Oil Combustion, (f) Non-ferrous Smelter, (g) Industrial Activities, (h) Soil, (i) Aged Sea Salt.

The concentration weighted PSCF model with the fractional source contribution results added further explanations of long-range transport of $PM_{2.5}$. PSCF values in the figure were divided into five categories, describing the frequency of trajectories. Cells with the highest probabilities were shaded in red, which indicates the most probable locations of the source contribution.

Secondary aerosols factors, Secondary Sulfate and Secondary Nitrate in this study were widely distributed from Shandong province to Jiangsu province where the east coast regions in China. Shandong, Hebei, Jiangsu, Henan, and Guangdong are the top five provinces with the greatest PM emissions in China in 2001 (Zhang et al. 2007). Among the 30 provinces in China, Shandong took part the greatest amount of SO_2 and NOx which were 5% and 3% of the national consumption-based emission, respectively and the statistics also showed Jiangsu followed in second place in 2007 (Zhao et al. 2015). These results go along with the study result (Jeong et al. 2011), which concluded that the Shandong peninsula is probably the major source of OC, EC, and $PM_{2.5}$. Several source apportionment studies in Korea have been suggested that Secondary Sulfate and Secondary Nitrate sources indicated high PSCF values in northeastern China (Jeong et al. 2017, Choi et al. 2013). The long-range transport of Industrial Activities, Soil, Oil Combustion, and Coal Combustion factors were also highly affected by Shandong province while sources like Soil and Coal Combustion were transported across North Korea. Long range source contributions of Non-ferrous Smelter, Mobile, and Aged Sea Salt did not specify certain regions but the source locations were rather distributed in several regions. Asian Dust (AD) events in Incheon (25 km from the sampling site) occurred in March, April, and May. Three times each in March and April while twice in May. The high level of $PM_{2.5}$ mass concentration in May might suggest the effect of AD events occurred in the same sampling month.

(a) Secondary Sulfate **(b) Secondary Nitrate**

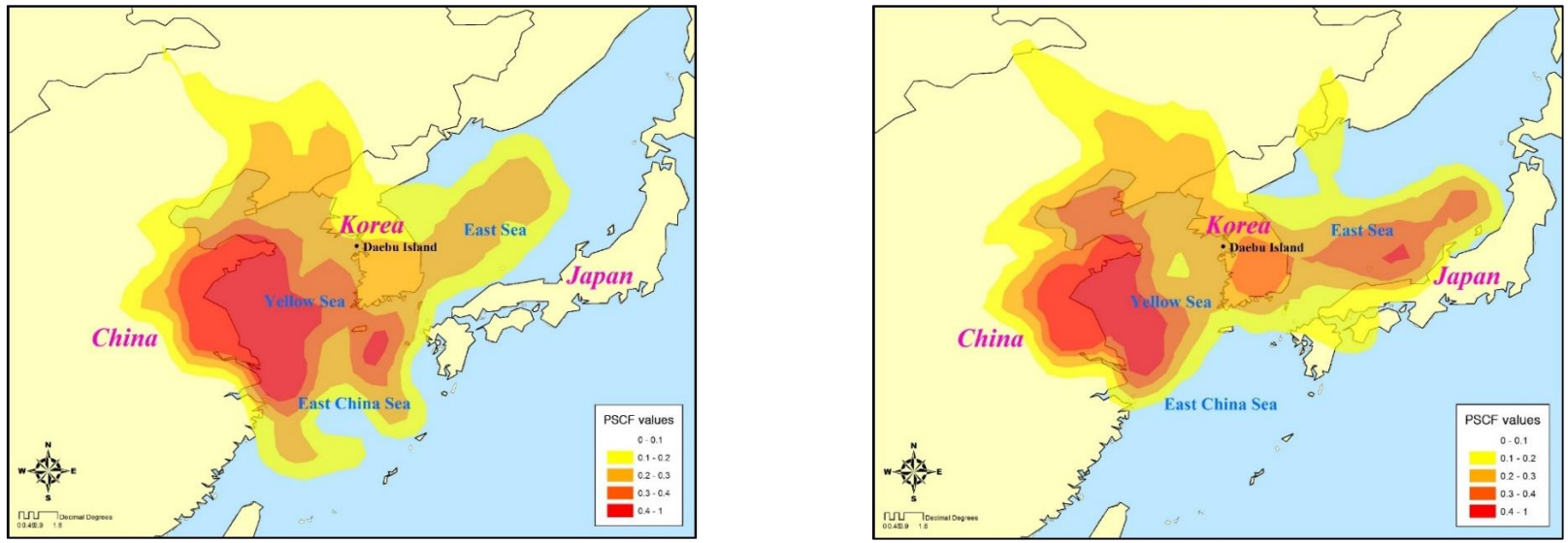

Fig. 2-9. PSCF results of (a) Secondary Sulfate factor (Right) and (b) Secondary Nitrate factor (Left), showing long-range transport from Chinese inland areas

2.4 Conclusions

For the source apportionment of $PM_{2.5}$ in Daebu Island, a total of 83 samples were analyzed with trace metals, ion species, and OC/EC. The PMF receptor model was performed by using the chemical speciation results as an input data set. The main conclusions from this study are described below.

(1) The monthly mass concentration of $PM_{2.5}$ was highest in May (46.5 ± 14.7 μg m^{-3}) and lowest in August (18.6 ± 8.1 μg m^{-3}). The average mass concentration during the whole sampling period (26.2 ± 13.2 μg m^{-3}) was much higher than the standard of US EPA (15 μg m^{-3}) as well as air quality standard of Korea (25 μg m^{-3}).

(2) The average concentration (0.21 μg m^{-3}) of potassium (K) was highest among the trace metal compounds and most of the other trace metal compounds showed similar monthly patterns with $PM_{2.5}$ mass concentrations. Among 4 ion compounds, sulfate (SO_4^{2-}) showed typical seasonal trends with the high concentration during summer and its average concentration contributed the largest amount when compared to other three ion species.

(3) The Organic Carbon (OC) and Elemental Carbon (EC) concentrations during the sampling period did not have much differences from the concentrations of megacity in Korea, Seoul. Through the average OC/EC ratio of 10.14, the plenty of Secondary Organic Aerosols (SOAs) formations were expected near the sampling site.

(4) Nine sources of $PM_{2.5}$ were identified in Daebu Island. Secondary Sulfate (29.0%), Mobile (22.0%), Secondary Nitrate (13.2%), Oil Combustion (10.1%), Coal Combustion (9.4%), Aged Sea Salt (7.9%), Soil (5.6%), Non-ferrous Smelter

(1.7%) and Industrial Activities (1.1%) were the nine sources from the PMF model. The factor of Secondary Sulfate suggested that the major form of secondary sulfate has a formation of ammonium sulfate ($(NH_4)_2SO_4$) with the high concentrations of SO_4^{2-} and NH_4^+.

(5) Hybrid receptor models with CPF and concentration weighted PSCF results revealed that Secondary Sulfate and Secondary Nitrate sources were likely to be transported from the east coast region of China where the high level of air pollution is expected. Other sources like Coal Combustion and Oil Combustion sources may attribute to both Industrial complexes in South Korea and Shandong peninsula in China.

From the study results, high contribution of secondary aerosols were expected with the long-range transport from overseas. Except the secondary aerosols contributions, mobile and combustion sources were the main anthropogenic sources affecting the contribution of particulate matters in Daebu Island. The other sources of $PM_{2.5}$ were expected to come from the natural such as aged sea salt and soil. These results supported that the sampling site has been affected by multiple sources as it could be inferred from the geographical position of the island.

References

Alexis, A, P Cox, A Lin, C Nguyen, and M Nystrom. 2005. "The California almanac of emissions and air quality." *California Air Resources Board, CA.*

Almeida, SM, CA Pio, MC Freitas, MA Reis, and MA Trancoso. 2006. "Approaching PM 2.5 and PM 2.5− 10 source apportionment by mass balance analysis, principal component analysis and particle size distribution." *Science of the Total Environment* no. 368 (2):663-674.

Ashbaugh, Lowell L, William C Malm, and Willy Z Sadeh. 1985. "A residence time probability analysis of sulfur concentrations at Grand Canyon National Park." *Atmospheric Environment (1967)* no. 19 (8):1263-1270.

Biggins, Peter DE, and Roy M Harrison. 1979. "Characterization and classification of atmospheric sulfates." *Journal of the Air Pollution Control Association* no. 29 (8):838-840.

Cabada, Juan C, Spyros N Pandis, Ramachandran Subramanian, Allen L Robinson, Andrea Polidori, and Barbara Turpin. 2004. "Estimating the secondary organic aerosol contribution to PM2. 5 using the EC tracer method special issue of aerosol science and technology on findings from the fine particulate matter supersites program." *Aerosol Science and Technology* no. 38 (S1):140-155.

Chan, YC, RW Simpson, GH Mctainsh, PD Vowles, DD Cohen, and GM Bailey. 1999. "Source apportionment of PM 2.5 and PM 10 aerosols in Brisbane (Australia) by receptor modelling." *Atmospheric Environment* no. 33 (19):3251-3268.

Choi, Jong-Kyu, Jong-Bae Heo, Soo-Jin Ban, Seung-Muk Yi, and Kyung-Duk Zoh. 2012. "Chemical characteristics of PM 2.5 aerosol in Incheon, Korea." *Atmospheric environment* no. 60:583-592.

Choi, Jong-kyu, Jong-Bae Heo, Soo-Jin Ban, Seung-Muk Yi, and Kyung-Duk Zoh. 2013. "Source apportionment of PM 2.5 at the coastal area in Korea." *Science of the Total Environment* no. 447:370-380.

Chow, Judith C, John G Watson, Eric M Fujita, Zhiqiang Lu, Douglas R Lawson, and Lowell L Ashbaugh. 1994. "Temporal and spatial variations of PM2. 5 and PM10 aerosol in the Southern California air quality study." *Atmospheric Environment* no. 28 (12):2061-2080.

Chu, Shao-Hang. 2005. "Stable estimate of primary OC/EC ratios in the EC tracer method." *Atmospheric Environment* no. 39 (8):1383-1392.

Cohen, David D, Jagoda Crawford, Eduard Stelcer, and Vuong Thu Bac. 2010.

"Characterisation and source apportionment of fine particulate sources at Hanoi from 2001 to 2008." *Atmospheric Environment* no. 44 (3):320-328.

Cohen, David D, Jarrod W Martin, and Graham M Bailey. 1993. "The determination of fine particle sulfur levels in the Wollongong, Newcastle and Sydney areas." *Clean Air: Journal of the Clean Air Society of Australia and New Zealand* no. 27 (2):63.

Coulibaly, Souleymane, Hiroki Minami, Maho Abe, Tomohiro Hasei, Nobuyuki Sera, Shigekazu Yamamoto, Kunihiro Funasaka, Daichi Asakawa, Masanari Watanabe, and Naoko Honda. 2015. "Seasonal fluctuations in air pollution in Dazaifu, Japan, and effect of long-range transport from mainland East Asia." *Biological and Pharmaceutical Bulletin* no. 38 (9):1395-1403.

Hallquist, Mattias, JC Wenger, Urs Baltensperger, Y Rudich, David Simpson, M Claeys, J Dommen, NM Donahue, C George, and AH Goldstein. 2009. "The formation, properties and impact of secondary organic aerosol: current and emerging issues." *Atmospheric Chemistry and Physics* no. 9 (14):5155-5236.

Han, JS, KJ Moon, SJ Lee, YJ Kim, SY Ryu, SS Cliff, and SM Yi. 2005. "Size-resolved source apportionment of ambient particles by positive matrix factorization." *Atmospheric Chemistry and Physics Discussions* no. 5 (4):5223-5252.

Han, JS, KJ Moon, SJ Lee, YJ Kim, SY Ryu, SS Cliff, and SM Yi. 2006. "Size-resolved source apportionment of ambient particles by positive matrix factorization at Gosan background site in East Asia." *Atmospheric Chemistry and Physics* no. 6 (1):211-223.

Harrison, Roy M, DJT Smith, and L Luhana. 1996. "Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK." *Environmental Science & Technology* no. 30 (3):825-832.

Henry, Ronald C, and Gary A Norris. 2002. "EPA Unmix 2.3 User Guide." *US Environmental Protection Agency: Washington, DC*.

Heo, J-B, PK Hopke, and S-M Yi. 2009. "Source apportionment of PM 2.5 in Seoul, Korea." *Atmospheric Chemistry and Physics* no. 9 (14):4957-4971.

Hopke, Philip K. 2003. "Recent developments in receptor modeling." *Journal of chemometrics* no. 17 (5):255-265.

Hyo, Yun Jin Joseph, and Avvari V Mohan. "A Comparative Study of the Dynamics of Innovation Systems in three Clusters from Korea and Malaysia."

Jeong, Ju-Hee, Zang-Ho Shon, Minsung Kang, Sang-Keun Song, Yoo-Keun Kim, Jinsoo Park, and Hyunjae Kim. 2017. "Comparison of source apportionment of PM 2.5 using receptor models in the main hub port city of East Asia: Busan." *Atmospheric Environment* no. 148:115-127.

Jeong, Ukkyo, Jhoon Kim, Hanlim Lee, Jinsang Jung, Young J Kim, Chul H Song, and Ja-Ho Koo. 2011. "Estimation of the contributions of long range transported aerosol in East Asia to carbonaceous aerosol and PM concentrations in Seoul, Korea using highly time resolved measurements: a PSCF model approach." *Journal of Environmental Monitoring* no. 13 (7):1905-1918.

Jeong, YeongJin, and InJo Hwang. 2015. "Source Apportionment of PM 2.5 in Gyeongsan Using the PMF Model." *Journal of Korean Society for Atmospheric Environment* no. 31 (6):508-519.

Kang, Choong-Min, Byung-Wook Kang, and Hak Sung Lee. 2006. "Source identification and trends in concentrations of gaseous and fine particulate principal species in Seoul, South Korea." *Journal of the Air & Waste Management Association* no. 56 (7):911-921.

Kim, Ki-Hyun, Dong-Sool Kim, and Tae-Jung Lee. 1997. "The temporal variabilities in the concentrations of airborne lead and its relationship to aerosol behavior." *Atmospheric Environment* no. 31 (20):3449-3458.

Kim, Ki-Hyun, and Min-Young Kim. 2003. "The effects of Asian Dust on particulate matter fractionation in Seoul, Korea during spring 2001." *Chemosphere* no. 51 (8):707-721.

Kim, Yoo Jung, Jung-Hun Woo, Young-Il Ma, Suhyang Kim, Jung Sik Nam, Hakyoung Sung, Ki-Chul Choi, Jihyun Seo, Jeong Su Kim, and Chang-Hee Kang. 2009. "Chemical characteristics of long-range transport aerosol at background sites in Korea." *Atmospheric Environment* no. 43 (34):5556-5566.

Lee, Taehyoung, Jinsoo Choi, Gangwoong Lee, Junyoung Ahn, Jin Soo Park, Samuel A Atwood, Misha Schurman, Yongjoo Choi, Yoomi Chung, and Jeffrey L Collett. 2015. "Characterization of aerosol composition, concentrations, and sources at Baengnyeong Island, Korea using an aerosol mass spectrometer." *Atmospheric Environment* no. 120:297-306.

Lim, Jong-Myoung, Jin-Hong Lee, Jong-Hwa Moon, Yong-Sam Chung, and Ki-Hyun Kim. 2010b. "Source apportionment of PM10 at a small industrial area using Positive Matrix Factorization." *Atmospheric Research* no. 95 (1):88-100.

Liu, Tengyu, Xinming Wang, Qihou Hu, Wei Deng, Yanli Zhang, Xiang Ding, X Fu, F Bernard, Zengxiang Zhang, and Shikun Lü. 2016. "Formation of secondary aerosols from gasoline vehicle exhaust when mixing with SO 2." *Atmospheric Chemistry and Physics* no. 16 (2):675-689.

Liu, Yan-Ju, Ting-Ting Zhang, Qing-Yang Liu, Ren-Jian Zhang, Zhen-Quan Sun, and Mei-Gen Zhang. 2014. "Seasonal variation of physical and chemical properties in TSP, PM10 and PM2. 5 at a roadside site in Beijing and their

influence on atmospheric visibility." *Aerosol Air Qual. Res* no. 14 (3):954-969.

Louie, Peter KK, John G Watson, Judith C Chow, Antony Chen, Della WM Sin, and Alexis KH Lau. 2005. "Seasonal characteristics and regional transport of PM 2.5 in Hong Kong." *Atmospheric Environment* no. 39 (9):1695-1710.

Manoli, E, D Voutsa, and C Samara. 2002. "Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece." *Atmospheric Environment* no. 36 (6):949-961.

Moon, KJ, JS Han, YS Ghim, and YJ Kim. 2008. "Source apportionment of fine carbonaceous particles by positive matrix factorization at Gosan background site in East Asia." *Environment international* no. 34 (5):654-664.

Moon, KJ, JS Han, BJ Kong, IR Jung, Steven S Cliff, Thomas A Cahill, and Kelvin D Perry. 2006. "Size-resolved source apportionment of ambient particles by positive matrix factorization at Gosan, Jeju Island during ACE-Asia." *Journal of Korean Society for Atmospheric Environment* no. 22 (5):590-603.

Norris, GA, R Duvall, SG Brown, and S Bai. 2014. EPA Positive Matrix Factorization (PMF) 5.0 fundamentals and User Guide Prepared for the US Environmental Protection Agency Office of Research and Development, Washington. DC EPA/600/R-14/108.

Oh, Hye-Ryun, Chang-Hoi Ho, Jinwon Kim, Deliang Chen, Seungmin Lee, Yong-Sang Choi, Lim-Seok Chang, and Chang-Keun Song. 2015. "Long-range transport of air pollutants originating in China: a possible major cause of multi-day high-PM 10 episodes during cold season in Seoul, Korea." *Atmospheric Environment* no. 109:23-30.

Oh, Mi-Seok, Tae-Jung Lee, and Dong-Sool Kim. 2009. "Source identification of ambient size-by-size particulate using the positive matrix factorization model on the border of Yongin and Suwon." *Journal of Korean Society for Atmospheric Environment* no. 25 (2):108-121.

Oh, Mi-Seok, Tae-Jung Lee, and Dong-Sool Kim. 2011. "Quantitative source apportionment of size-segregated particulate matter at urbanized local site in Korea." *Aerosol and Air Quality Resarch* no. 11 (3):247-264.

Paatero, Pentti. 1997. "Least squares formulation of robust non-negative factor analysis." *Chemometrics and intelligent laboratory systems* no. 37 (1):23-35.

Paatero, Pentti, and Unto Tapper. 1994. "Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values." *Environmetrics* no. 5 (2):111-126.

Pace, TG, and JG Watson. 1987. Protocol for applying and validating the CMB (chemical mass balance) model. Environmental Protection Agency,

Research Triangle Park, NC (USA). Monitoring and Data Analysis Div.

Park, Seung S, Young J Kim, and Kochy Fung. 2001. "Characteristics of PM 2.5 carbonaceous aerosol in the Sihwa industrial area, Korea." *Atmospheric Environment* no. 35 (4):657-665.

Raaschou-Nielsen, Ole, Zorana J Andersen, Rob Beelen, Evangelia Samoli, Massimo Stafoggia, Gudrun Weinmayr, Barbara Hoffmann, Paul Fischer, Mark J Nieuwenhuijsen, and Bert Brunekreef. 2013. "Air pollution and lung cancer incidence in 17 European cohorts: prospective analyses from the European Study of Cohorts for Air Pollution Effects (ESCAPE)." *The lancet oncology* no. 14 (9):813-822.

Samara, C, Th Kouimtzis, R Tsitouridou, G Kanias, and V Simeonov. 2003. "Chemical mass balance source apportionment of PM 10 in an industrialized urban area of Northern Greece." *Atmospheric environment* no. 37 (1):41-54.

Stafoggia, Massimo, Alexandra Schneider, Josef Cyrys, Evangelia Samoli, Zorana Jovanovic Andersen, Getahun Bero Bedada, Tom Bellander, Giorgio Cattani, Konstantinos Eleftheriadis, and Annunziata Faustini. 2017. "Association between short-term exposure to ultrafine particles and mortality in eight European urban areas." *Epidemiology*.

Sun, Yele, Guoshun Zhuang, Ying Wang, Lihui Han, Jinghua Guo, Mo Dan, Wenjie Zhang, Zifa Wang, and Zhengping Hao. 2004. "The air-borne particulate pollution in Beijing—concentration, composition, distribution and sources." *Atmospheric Environment* no. 38 (35):5991-6004.

Swietlicki, Erik, Sanjiv Puri, Hans-Christen Hansson, and Hans Edner. 1996. "Urban air pollution source apportionment using a combination of aerosol and gas monitoring techniques." *Atmospheric Environment* no. 30 (15):2795-2809.

Thurston, George D, and John D Spengler. 1985. "A multivariate assessment of meteorological influences on inhalable particle source impacts." *Journal of Climate and applied meteorology* no. 24 (11):1245-1256.

Uberol, Mohit, and Farhang Shadman. 1991. "High-temperature removal of cadmium compounds using solid sorbents." *Environmental Science and Technology* no. 25 (7):1285-1289.

Wang, SX, Bin Zhao, SY Cai, Z Klimont, CP Nielsen, T Morikawa, JH Woo, Y Kim, X Fu, and JY Xu. 2014. "Emission trends and mitigation options for air pollutants in East Asia." *Atmospheric Chemistry and Physics* no. 14 (13):6571-6603.

Wang, Xiaobin, O Oenema, WB Hoogmoed, UD Perdok, and Dianxiong Cai. 2006. "Dust storm erosion and its impact on soil carbon and nitrogen losses in northern China." *Catena* no. 66 (3):221-227.

Wang, Yan, Liuhua Shi, Mihye Lee, Pengfei Liu, Qian Di, Antonella Zanobetti, and

Joel D Schwartz. 2017. "Long-term exposure to PM2. 5 and mortality among older adults in the Southeastern US." *Epidemiology*.

Yi, Seung-Muk, and InJo Hwang. 2014. "Source Identification and Estimation of Source Apportionment for Ambient PM 10 in Seoul, Korea." *Asian J. Atmos. Environ* no. 8 (3):115-125.

Zhang, Qiang, David G Streets, Kebin He, and Zbigniew Klimont. 2007. "Major components of China? s anthropogenic primary particulate emissions." *Environmental Research Letters* no. 2 (4):045027.

Zhao, HY, Q Zhang, DB Guan, SJ Davis, Z Liu, H Huo, JT Lin, WD Liu, and KB He. 2015. "Assessment of China's virtual air pollution transport embodied in trade by using a consumption-based emission inventory." *Atmospheric Chemistry and Physics* no. 15 (10):5443-5456.

Supplementary Materials

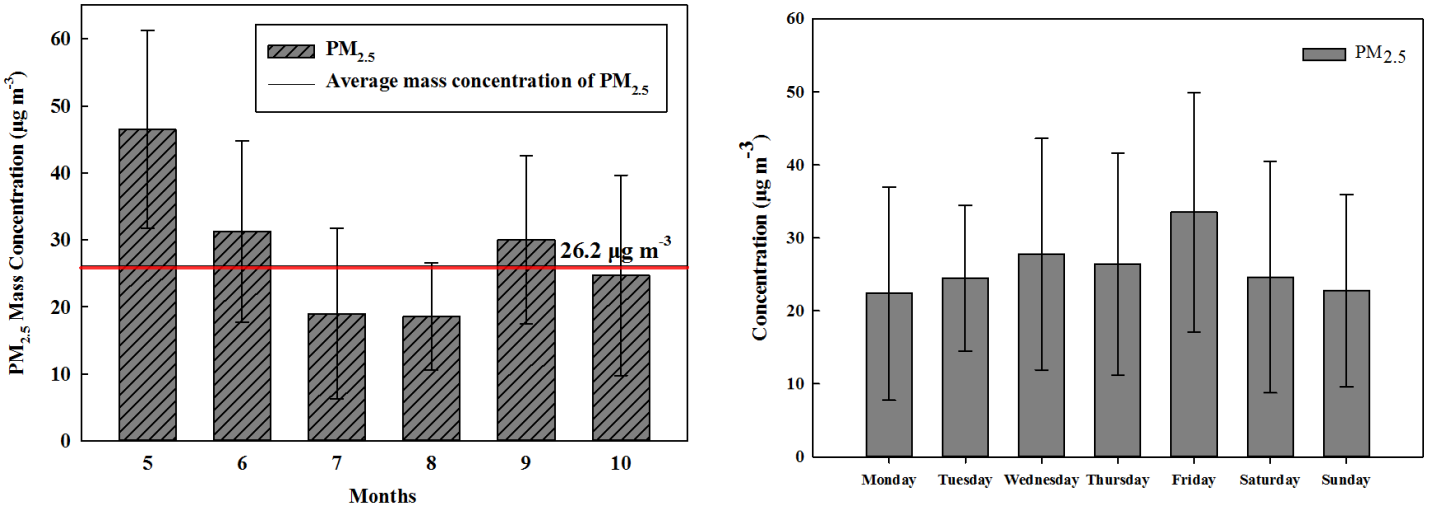

Fig. S2-1. Monthly mass concentrations of $PM_{2.5}$ in the sampling site (Right) and $PM_{2.5}$ mass concentrations of weekday and weekend in the sampling period (Left)

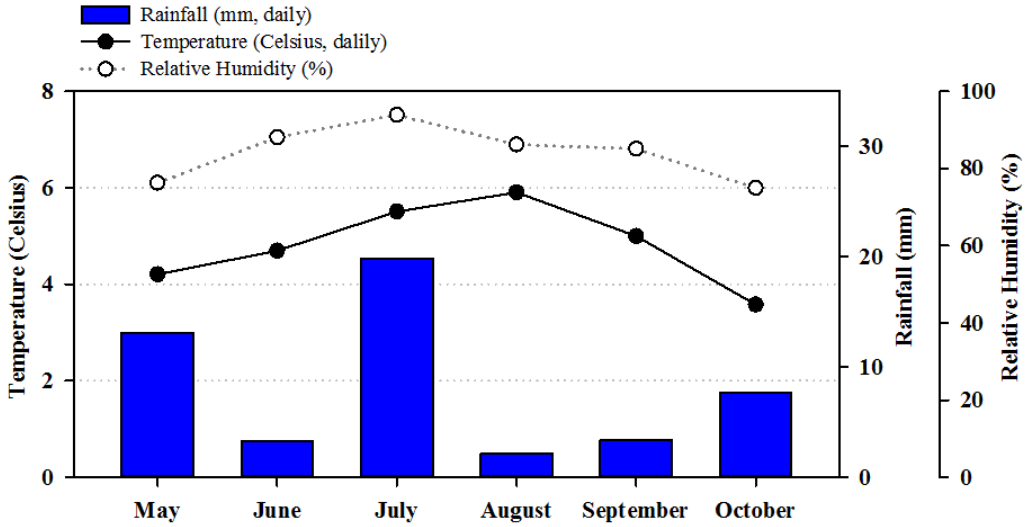

Fig. S2-2. Monthly trend of daily rainfall (mm), temperature (°C), and relative humidity (%) in May to October in 2016. Rainfall and temperature data was from AWS in Daebu Island, while relative humidity data was replaced with AWS data from Incheon.

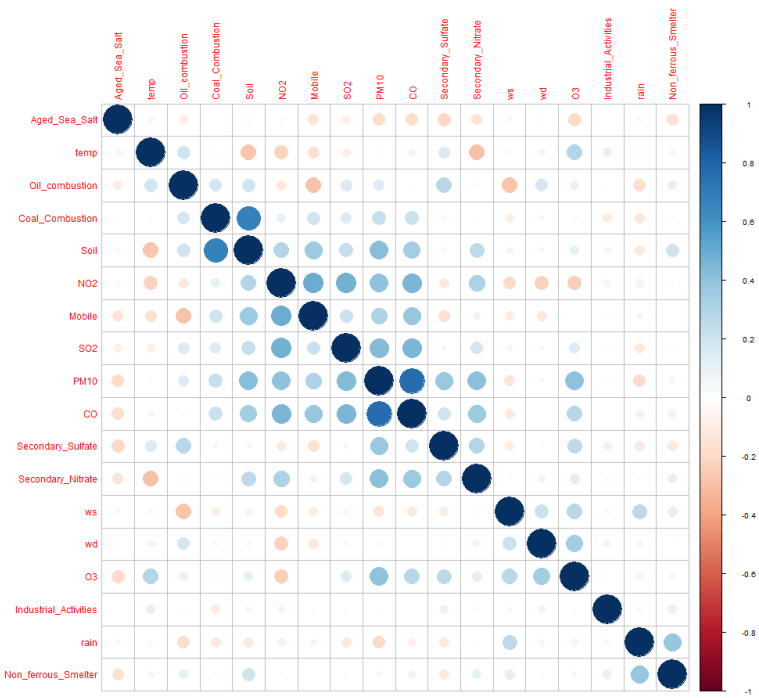

Fig. S2-3. Correlation coefficients matrix between source contributions and meteorological data in Daebu Island, Korea

Table S2-1. Ion Chromatography (Dionex Co., DX-1100, USA) operations for anion and cation in this study

	Anion	Cation
Instrument	DX-1100 (Dionex)	
Column	Ionpac (AS14A, 4×250 mm)	Ionpac (CS12A, 4×250 mm)
Eluent	3.5 mM Sodium Carbonate + 1.0 mM Sodium Bicarbonate	20 mM Methane Sulfonic Acid (MSA)
Flow rate	1.2 mL/min	1.0 mL/min
Suppressor	Dionex™ AERS 500 (4 mm), (Part Number : 082540)	Dionex™ SC-CSRS 300 (4 mm), (Part Number : 067530)
Standard Solution	Dionex™ Seven Anion Standard Ⅱ (Part Number : 057590)	Dionex™ Six Cation Standard Ⅱ (Part Number : 046070)

Anions : Cl^-, NO_3^-, and SO_4^{2-}
Cations : NH_4^+

Table S2-2. Analytical condition of OC/EC aerosol analyzer (Sunset Laboratory Inc., USA) operated in this study

Step		Carrier Gas	Ramp Time (seconds)	Program Temperature (˚C)
OC	Step 1.	Helium (He)	80	310
	Step 2.	Helium (He)	60	475
	Step 3.	Helium (He)	60	650
	Step 4.	Helium (He)	90	870
		Helium (He)	Oven heaters are turned off to cool oven	
EC	Step 5.	2% Ox in He	45	550
	Step 6.	2% Ox in He	45	625
	Step 7.	2% Ox in He	45	700
	Step 8.	2% Ox in He	45	775
	Step 9.	2% Ox in He	45	850
	Step 10.	2% Ox in He	120	870
		Cal Gas + Helium/Ox	External Std. Calibration and cool-down	

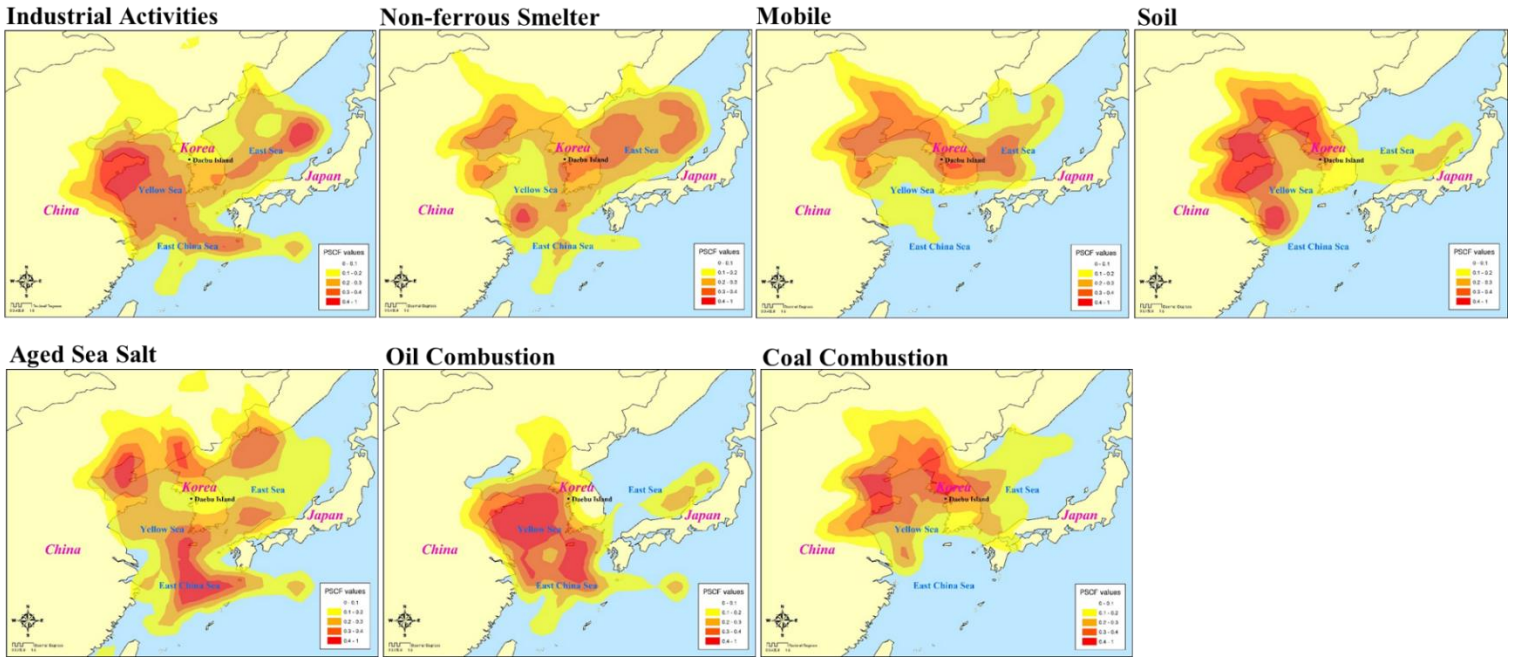

Fig. S2-4. PSCF plots for the factor of Industrial Activities, Non-ferrous Smelter, Mobile, Soil, Aged Sea Salt, Oil Combustion, and Coal Combustion

Abstract

Chapter 3. Characteristics of organic compounds and source apportionment using Principal Component Analysis (PCA) in Daebu Island, Korea

Sun-Hye Kim

Department of Environmental Health Sciences

Graduate School of Public Health

Seoul National University

Organic compounds in fine particulate matters ($PM_{2.5}$) were known to have deleterious effects on the human body and therefore identification of individual organic compounds is important for the managing air pollution sources in view of health of the community. Stable organic compounds have been used as fingerprints to identify specific source distributions and the analytical data set of organics have been also considered to be very useful when performing receptor models.

Principal Component Analysis (PCA) was performed with filter-based $PM_{2.5}$ data including organic compounds and inorganic elements from Daebu Island, Korea. Organic samples were collected through a high-volume air sampler from May 27 to October 30 in 2016. The carbonaceous characteristics of $PM_{2.5}$ were determined with Water-Soluble Organic Carbon (WSOC), Secondary Organic Carbon (SOC), Primary Organic Carbon (POC), Water-Insoluble Organic Carbon (WIOC) with 77

species of individual organic compounds. The organic characteristic of $PM_{2.5}$ in this site was discussed with PAHs diagnostic ratio, Carbon Preference Index (CPI) value, percentage of wax n-Alkanes (WNA%) with their seasonal patterns as well as the individual organic compounds concentrations.

Due to the limitation on the size of filter-based sample (n=38), Principal Component Analysis (PCA) was adopted for source apportionment method. Inorganic element data, previously discussed in chapter 2 was coupled with organic compounds data to produce source factors from Principal Component Analysis (PCA). A total of six factors, Secondary Organic Aerosols 1 (SOAs 1, 38.568%), Combustion related sources (20.170%), Secondary Organic Aerosols 2 (SOAs 2, 10.191%), Secondary inorganic factor (7.434%), Biomass burning (5.833%), and Industrial sources (4.455%) were identified through PCA result with especially high contributions to secondary aerosols and combustion sources. Unlike the factor of SOAs 1, SOAs 2 showed high correlation with WIOC, which was indicative of the contribution of anthropogenic VOCs.

Keywords: Fine particulate matter ($PM_{2.5}$), Water-Soluble Organic Carbon (WSOC), Secondary Organic Carbon (SOC), Primary Organic Carbon (POC), Water-Insoluble Organic Carbon (WIOC), Organic molecular markers, Principal Component Analysis (PCA)

Student Number: 2015-24104

3.1 Introduction

The chemical composition of fine particulate matter ($PM_{2.5}$) is greatly associated with where it has been originated (Ram, Sarin, and Tripathi 2012) as well as the atmospheric environment when the fine particles were formed. The anthropogenic activity is one of great emission sources of toxic fine particles that can badly affect the human body (Koch 2000) and therefore the reduction of those compounds has become a great concern in the world.

Effective control of toxic chemicals in aerosols can be done with the successful national air pollution policy when element speciation of aerosols were extensively used as a key to identify potential sources (Cass 1998). In the case of lead (Pb), which was once used as an indicator of leaded gasoline is now completely replaced with lead-free fuels in many countries (Cass 1998). However, the removal of such chemical requires more elaborate tracer methods that can replace certain trace metal markers. Difficulty in differentiating common sources was another problem since some sources emit the same kind of inorganic elements. For example, potassium (K^+) has been demonstrated that inorganic tracer of biomass burning in many studies (Andreae 1983, Calloway et al. 1989, Turn et al. 1997). However, many inorganic elements including potassium practically originate from multiple sources and therefore the source identification technique solely based on a certain inorganic compound have not been recommended for the reasonable assumption of air pollution sources (Lin, Lee, and Eatough 2010, Zhang et al. 2008).

Distinctive organic compounds, which are not easily degradable and reactive in the atmosphere became powerful fingerprints (i.e. levoglucosan for wood burning sources) to improve identification ability with the development of analytical methods

(Schauer et al. 1996). Several studies have been suggested that organic molecular trace method is the powerful tool for identifying specific source contributions (i.e. coronene and benzo[ghi]perlebe concentrations are unique markers for motor vehicle emissions) and thereby the methods have been applied in receptor models for the improvement of source identifications. Organic molecular markers take advantage of distinguishing specific source contributions compare to inorganic elemental markers. The organic compounds itself have been accepted as good indicators but organic molecular diagnostic ratios also have been used for separating mixed sources, for instance, PAHs diagnostic ratios enable distinguishing gasoline emissions from diesel emissions. These organic compounds should be the characteristics of specific sources but not others. They must react slowly enough in the atmosphere that they should be survived while they are transported from origins to receptor air monitoring stations. Organic molecular tracer method uses unique organic chemical compounds that are emitted from certain sources (Cass 1998). The compounds which were chosen as key tracers also must be the ones that are not formed by atmospheric chemical reactions and they must not evaporate into the gas phase over the transportation time.

Carbonaceous species in $PM_{2.5}$ can be largely categorized into two groups, which are Organic Carbon (OC) and Elemental Carbon (EC) by their relative carbon contents (Molnár et al. 1999) or the thermal methodology under different degradation temperature. Organic carbon in ambient particles often emitted from various sources whereas EC, which is not volatile in ambient temperature generally comes from the thermal combustion of OC (Schauer et al. 2003). This emission characteristic enables using signature information by inferring source contributions from OC to EC ratio. OC in the atmospheric particle can be either Primary Organic Carbon (POC) or

Secondary Organic Carbon (SOC) depending on its formation processes. As the name indicates, POC directly emitted from sources while SOC formation requires photo-oxidation reactions from precursor gases (Rogge, Mazurek, et al. 1993, Turpin and Huntzicker 1995). OC and EC can also be divided into various carbonaceous organic groups by their functional groups, which are PAHs, n-Alkanes, n-Alkanoic acids, Dicarboxylic acids (DCAs) and Sugars though not all organic species have not yet identified.

This study evaluated the sources of $PM_{2.5}$ in Daebu Island, Korea with the organic compounds. Water-Soluble Organic Carbon (WSOC) of the sampling site was determined using TOC-V CPH total carbon analyzer (Shimadzu, Japan) as well as Water-Insoluble Organic Carbon (WIOC). The concentration of SOC and POC were calculated based on EC tracer method with Deming regression. Chemical speciation data of 77 individual organic compounds and 12 elemental constituents were combined to source identification based on the Principal Component Analysis (PCA).

3.2 Methodology

3.2.1 Chemical speciation

Organic compounds

$PM_{2.5}$ organic compounds samples (n=38) were collected every four-day from May 27 to October 30 in 2016 using high volume air samplers. The sampling site is located in the center of Daebu Island (126°35′E, 37°15’N), South Korea. The specific description of the sampling site and OC/EC, ions and trace metal analysis can be found elsewhere (Chapter 2. in this study). Organic compound samples were

collected on the Quartz microfiber filters (Whatman™, QMA 1851-865, UK) while the particles bigger than 2.5 micrometers were filtered using Impactor (TISCH, TE-230-QZ, USA). The preparation of Quartz microfiber filters was proceeded at 450 C° for 12 hours in the furnace to lower the carbon blank value. $PM_{2.5}$ collected filters are stored in the thermos-hygrostat for 24 hours and then kept in the freezer before starting sample analysis. Extraction of the samples is obtained by DCM: MeOH (3:1) mixture solvent through ultrasonication for 30 min. The ultrasonic agitation process is repeated twice successively. The filters are then spiked with 250 μL surrogate standard mixture for the sample recovery calibration. Extracted sample solvent is filtered using Syringe filters (PALL science, 0.45μm pore size) and then concentrated using Turbovap Ⅱ (Caliper Life Sciences) in a volume of 500μL in MS analyzed vials (5190-2280, Agilent, USA). Samples were analyzed for 77 of individual organic compounds: A total 31 of polar compounds and 46 of non-polar compounds. For polar compounds samples, derivatization processes were performed by adding 50 μl of N,O-Bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane and 50 μl of Pyridine, respectively. This process transformed the chemical structures of polar compounds by removing the polar OH, NH, and SH groups of chemicals, which enables them to be more easily volatilized in GC-MS separation. (Wang et al. 2012). GC-MS (Agilent Technologies, 7890A, 5975C, USA) was then used for the chemical speciation of organic samples. A 30 m of GC column (DB-5MS 30m, 0.25mm, 0.25μm, Agilent Technologies) was used. The temperature program was functioned at 60 C° for 1 min initially and then increased to a final temperature at a rate of 6 C° min^{-1}. The isothermal pause lasted for 15 min at a temperature of 310 C°. Helium is injected a splitless port at a gas flow rate of 1 mL m^{-1} as a carrier gas. The solvent delay time was set to 8 min (Supplementary Table S3-1).

Table 3-1. Targeted organic groups with individual organic compounds and their abbreviations used in this study

Non-Polar compounds		Polar compounds		
PAHs	n-Alkanes	n-Alkanoic acids	Dicarboxylic acids	Sugars
Phenanthrene, PHEN	n-Eicosane, C20	Octanoic acid, C8	Malonic acid, C3	D-(-)-Arabinose
Anthracene, ANTHR	n-Henicosane, C21	Nonanoic acid, C9	Methylmalonic acid, iC4	D-(-)-Ribose
Fluranthene, FLT	n-Docosane, C22	Decanoic acid, C10	Maleic acid, M	Levoglucosan
Pyrene, PYR	n-Tricosane, C23	Undecanoinc acid, C11	Succinic acid, C4	D-(+)-Xylose
Benz[a]anthracene, BaA	n-Tetracosane, C24	Lauric acid, C12	Methylsuccinic acid, iC5	D-(-)-Fructose
Chrysene, CHR	n-Pentacosane, C25	Tridecanoic acid, C13	Methylmaleic acid, mM	D-(+)-Mannose
Benzo[b]fluoranthene, BbF	n-Hexacosane, C26	Myristic acid, C14	Fumaric acid, F	D-(+) Galactose
Benzo[e]pyrene, BeP	n-Heptacosane,C27	Pentadecanoic acid, C15	Glutaric acid, C5	D-(+)-Glucose
Benzo[a]pyrene, BaP	n-Octacosane, C28	Palmitic acid, C16	2-methylglutaric acid, iC6	Sucrose
Perylene, PER	n-Nonacosane, C29	Heptadecanoic acid, C17	D-Malic acid, hC4	D-(+)-Maltose
Indeno[1,2,3-cd]pyrene, IND	n-Triacontane, C30	Stearic acid, C18	Adipic acid, C6	
Dibenz[a,h]anthracene, DahA	n-Hentriacontane, C31	Eicosanoic acid, C20	Pimelic acid, C7	
Benzo[ghi]perylene, BghiP	n-Dotriacontane, C32	Heneicosanoic acid, C21	Phthalic acid, Ph	
Coronene, COR	n-Tritriacontane, C33	Docosanoic acid, C22	Suberic acid, C8	
	n-Tetratriacontane, C34	Tricosanoic acid, C23	Iso-phthalic acid, iPh	
	n-Pentatriacontane, C35	Tetracosanoic acid, C24	Tere-phthalic acid, TPh	
	n-Hexatriacontane, C36	Elaidic acid, *trans*-C18	Azelaic acid, C9	
			Sebacic acid, C10	
			Undecanedionic acid, C11	

PAHs : Polycyclic Aromatic Hydrocarbons

Water Soluble Organic Carbons (WSOC)

$PM_{2.5}$ samples for WSOC were collected using Quartz fiber filters (Whatman™, 47mm). After determining the OC and EC concentration in the Quartz fiber filter, rest of the filters were extracted with distilled deionized water (18.2 MΩ cm). Extraction bottles were used for transferring filter solutions and prepared in a furnace before analysis (450 C°, 12 hours). After that, the sonication process was performed for 1 hour. Before WSOC samples were determined with TOC-V CPH total carbon analyzer (Shimadzu, Japan), extracted solutions were filtered using disposable syringe filters (Advantec, HP045AN, 0.45µm pore size) to remove suspended particles in solution. TC (Total Carbon) and IC (Inorganic Carbon) were measured simultaneously and the value of IC was subtracted from TC to obtain the value of water-soluble total organic carbon. For TC standard solution, 2.125g of reagent grade potassium hydrogen phthalate (99.5 – 100.2%, Samchun Chemicals) was transferred to a 1 L volumetric flask to dissolve in distilled water for preparing the stock solution with the carbon concentration of 1000 mg C/L. IC stock solution was made with accurately weighed 3.50 g of sodium hydrogen carbonate (99.0%, Samchun Chemicals) and 4.41 g of sodium carbonate (99.5% -100.5%, Sigma-aldrich), transfer the weighed materials were dissolved in 1L of DI water. Total 83 samples were identified with TOC-V CPH total carbon analyzer. Water-soluble organic carbon compounds have been widely accepted as indicators of Secondary Organic Aerosols (SOAs) while they contain both primary and secondary aerosols. The average WSOC concentration in $PM_{2.5}$ was identified as 3.06 ± 2.28 µg m^{-3}. High WSOC/OC ratio during the summer period can be explained by higher chances of photochemical reactions during the summer season (Miyazaki et al. 2006). The average WSOC/OC ratios in spring, summer and winter concentration were 0.51 ± 0.19, 0.59 ± 0.10 and 0.43 ± 0.25, respectively. The average contribution of WSOC

to OC was identified with more than half of the total OC concentrations (0.53 ± 0.35). While NO_3^- and SO_4^{2-} were categorized as water-soluble inorganic ions, relatively high correlation coefficient values with WSOC were obtained from SPSS software, which were determined as 0.441 and 0.295 for the NO_3^- and SO_4^{2-}, respectively (Table 3-10). From the results, it can be concluded that substantial portions of the WSOC in $PM_{2.5}$ were composed of Secondary Organic Aerosols (SOAs) since the formation process of NO_3^- and SO_4^{2-} were similar to that of SOAs. The SOC and WSOC showed the correlation value of 0.296, which is considered as a moderate correlation.

Secondary Organic Carbon (SOC) and Primary Organic Carbon (POC)

The direct estimation of Secondary Organic Carbon (SOC) and Primary Organic Carbon (POC) was difficult owing to its complex characteristics, whereas quantifying Total Organic Carbon (TOC) is relatively simple. Instead of direct estimation of those compounds, indirect way to calculate SOC and POC has been suggested in former studies, which is known as an EC tracer method (Gelencsér et al. 2007). This method is based on the hypothesis that inert EC, which is stable and less reactive in the atmosphere has common emission sources (i.e. combustion) with POC. Since it assumes good correlations between two compounds, POC can be indirectly inferred with EC concentration (Lin et al. 2009). With the determined OC and EC data set, Secondary Organic Carbon (SOC) concentrations were inferred using the equation (1) below.

$$SOC = OC_{(TOC)} - ([OC/EC]_{primary} \times EC + OC_{non\text{-}combustion}) \quad (1)$$

$$POC = OC_{(TOC)} - SOC \quad (2)$$

The equation (1) assumes that measured OC is emitted from both primary sources and secondary sources while primary OC is then comes from both non-combustion OC and combustion OC. Prior EC tracer methods have difficulties in reflecting possible errors in measured OC and EC values (Cornbleet and Gochman 1979, Saylor, Edgerton, and Hartsell 2006) and therefore for assuming possible errors in the measurement values, regression method of Deming (1943) was adopted in this study to better estimate the variables of $[OC/EC]_{primary}$ and $OC_{non\text{-}combustion}$ (Snyder et al. 2009). The $[OC/EC]_{primary}$ and $OC_{non\text{-}combustion}$ in this analysis showed the values of 4.181 and 0.237, respectively.

To resolve the equation, OC and EC concentration data were obtained by TOT (Thermal-Optical-Transmittance) method with NIOSH 5040 protocol. From this method, a total average concentration of SOC (2.80 ± 1.21 μg m^{-3}) and POC (3.15 ± 3.07 μg m^{-3}) were obtained. The monthly concentration of SOC, POC, WSOC, and WIOC were described in the Fig.3-1.

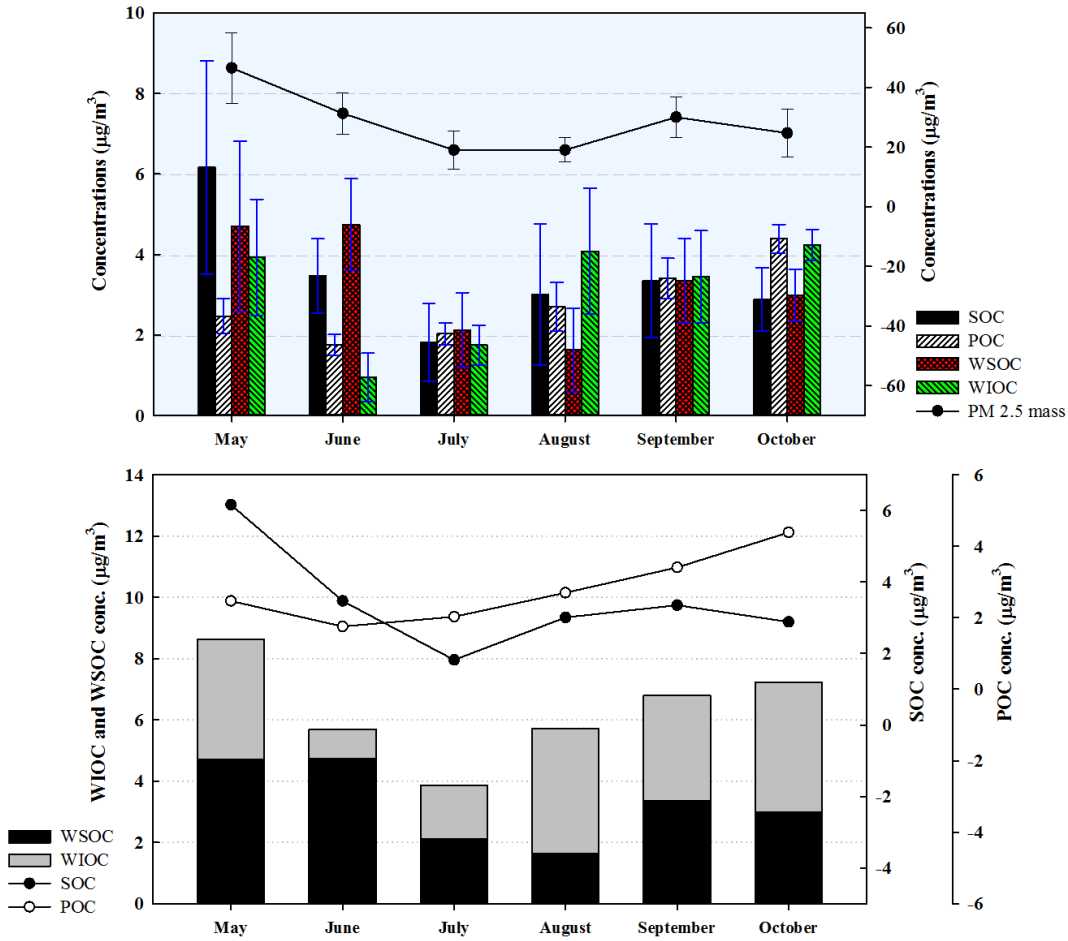

Fig. 3-1. (a) Monthly trends with SOC, POC, WSOC, and WIOC during the sampling period and (b) Monthly mass fraction concentrations of EC, SOC, and POC. Error bars are presented using standard error of mean values (± 95% confidence interval)

The highest SOC concentration in May (6.16 ± 3.30 μg m^{-3}) was more than three times the lowest concentration in July (1.82 ± 1.90 μg m^{-3}). Though WSOC concentration was highest in June (4.74 ± 2.24 μg m^{-3}), not much difference with the second highest concentration in May (4.70 ± 2.64 μg m^{-3}) was identified. It

seemed clear that the monthly trend of SOC and WSOC showed the similar concentration pattern with $PM_{2.5}$: relatively high concentration trend in spring (May) and autumn (September and October) with low concentrations in summer season (June to August). A good agreement with $PM_{2.5}$ mass concentration corroborates the large amount of SOC and WSOC contributions during the overall sampling period.

Meanwhile, both POC and WIOC concentration were peaked in October (POC: 4.39 ± 1.35 μg $m^{-3}$and WIOC: 4.24 ± 1.43 μg m^{-3}) whereas lowest in June (POC: 1.76 ± 0.51 μg m^{-3} and WIOC: 0.95 ± 1.20 μg m^{-3}) with the general increasing mass trend. Generally, most of (more than 90%) the POC is known to be water-insoluble (Miyazaki et al. 2006) and the concentration trend of both group in the figure seemed to have strong correlations, however, the PCA result in this study suggested high possibility of large contribution in water-insoluble characteristics to secondary organic matters. Even with the lowest $PM_{2.5}$ mass concentration in July, both POC and WIOC had increased compare to May, which suggested the huge contribution of anthropogenic combustion sources in July.

Quality Assurance and Quality Control (QA/QC).

For the assurance of trustworthy data, quality assurance and quality control (QA/QC) process have been done with every data set and the results of QA/QC in this study were described in the tables below with supplementary materials (Table S3-3 and Table S3-4). WSOC analysis with TOC was proceeded by injecting 100 μL every sample solution. Same amount of solution was injected three times and the averaged two-time values were used if the analysis values were within criteria range (standard

deviation of ± 0.1 and confidence level of ± 2%). The R^2 values of TC and IC calibration curve were 0.999 and 0.997, respectively.

The QA/QC procedures for organic compounds were proceeded using internal standardization and standard reference material 1649b (Urban dust, National Institute of Standard and Technology (NIST), USA). Internal standardization method was applied for each of individual organic compound to reflect sample recovery. Obtained ratio of targeted sample peak area to internal standard peak area ($A_{targeted}/A_{IS}$) was assigned as Y axis, substituting X axis with the concentration of individual organic compounds (Fig. S3-7, S3-8, S3-9, S3-10, and S3-11). The mass concentrations of each compound were obtained by substituting the response ratio of each sample (A_{sample}/A_{IS}) to Y values. Surrogate standards were added in every process of sample extraction to monitor possible loss from experiment steps and the recovery rate was suggested with 7 replicated samples. (Table 3-2, 3-3, and 3-4). For the recovery of PAHs, Standard Reference Material 1649b (National Institute of Standard Technology NIST, Urban dust) was also used for additional analysis of fine particulate matters. The recovery values of PAHs using SRM 1649b (n=6) were extracted in organic solvent and injected in the instrument exactly the same way that $PM_{2.5}$ samples were treated. The recovery of PAHs compounds in SRM ranged from 44% to 142% when using 100 mg of SRM materials.

Table 3-2. Summary of PAHs recovery test using SRM (Standard Reference Material) NIST 1649b Urban Dust and Internal standardization method

PAHs Compounds	Overall recovery test					
	SRM NIST 1649b Urban Dust (n=6)[a)]				**Internal standardization method (n=7)**	**MDL (ng/μL)**
	Certified Value (mg/kg)	Measured Value (mg/kg)	Recovery (%)	RSD[b)] (%)	Recovery (%)	
Phenanthrene	4.03 ± 0.06	2.59 ± 0.19	55.02 ± 4.60	8.35	82.30 ± 31.15	0.007
Anthracene	0.41 ± 0.00	0.66 ± 0.04	138.65 ± 10.68	7.70	84.27 ± 31.87	0.014
Fluoranthene	6.24 ± 0.08	4.26 ± 0.32	58.54 ± 5.07	8.67	93.83 ± 35.50	0.008
Pyrene	4.98 ± 0.14	3.50 ± 0.26	60.26 ± 5.28	8.76	101.57 ± 38.43	0.01
Benz[a]anthracene	2.35 ± 0.12	1.40 ± 0.11	51.17 ± 4.72	9.23	81.66 ± 30.89	0.012
Chrysene	3.05 ± 0.03	3.11 ± 0.24	87.42 ± 7.73	8.84	88.37 ± 33.44	0.009
Benzo[b]fluoranthene	6.18 ± 0.18	4.54 ± 0.32	62.99 ± 5.11	8.11	79.03 ± 29.90	0.007
Benzo[e]pyrene	2.97 ± 0.05	2.49 ± 0.18	71.68 ± 5.96	8.31	80.93 ± 30.63	0.003
Benzo[a]pyrene	2.81 ± 0.38	1.45 ± 0.11	44.19 ± 4.02	9.10	76.43 ± 28.93	0.012
Perylene	0.61 ± 0.01	0.49 ± 0.07	68.77 ± 12.18	17.71	76.90 ± 29.15	0.009
Indeno[1,2,3-cd]pyrene	2.89 ± 0.16	2.41 ± 0.13	71.57 ± 4.36	6.09	93.72 ± 35.48	0.008
Dibenz[a,h]anthracene	0.29 ± 0.00	0.49 ± 0.02	142.48 ± 8.15	5.72	96.16 ± 36.42	0.007
Benzo[ghi]perylene	3.97 ± 0.04	2.91 ± 0.21	62.85 ± 5.30	8.43	101.24 ± 38.32	0.013
Coronene	3.16 ± 0.05	2.03 ± 0.70	55.19 ± 22.04	39.93	79.89 ± 30.35	N.A[c)]

[a)] 100 mg of Standard Reference Material (SRM) 1649b was used for each replicate sample
[b)] RSD (%) =Standard deviation/Average × 100
[c)] N.A = Not Available

Table 3-3. Recovery rates of n-Alkanes by using internal standard method with 7 of replicates

Compounds	Calibration curve Recovery (%)	MDL (ng/μL)
n-Eicosane, C20	112.63 ± 79.64	0.012
n-Henicosane, C21	105.55 ± 67.49	0.016
n-Docosane, C22	101.02 ± 50.66	0.014
n-Tricosane, C23	108.22 ± 49.58	0.017
n-Tetracosane, C24	105.80 ± 43.51	0.01
n-Pentacosane, C25	104.83 ± 43.07	0.012
n-Hexacosane, C26	105.21 ± 43.40	0.009
n-Heptacosane, C27	108.73 ± 45.18	0.007
n-Octacosane, C28	102.76 ± 44.99	0.009
n-Nonacosane, C29	98.62 ± 40.93	0.01
n-Triacontane, C30	101.83 ± 44.02	0.006
n-Hentriacontane, C31	101.67 ± 45.62	0.011
n-Dotriacontane, C32	112.05 ± 59.16	0.01
n-Tritriacontane, C33	148.07 ± 92.16	0.008
n-Tetratriacontane, C34	222.55 ± 179.92	0.038
n-Pentatriacontane, C35	266.42 ± 229.24	N.A
n-Hexatriacontane, C36	465.98 ± 251.81	N.A

N.A : Not Available. The MDL value for C35 and C36 were not identified in this study.

Table 3-4. Summary table of internal standard method recoveries for Polar compound group (n-Alkanoic acids, Dicarboxylic acids, and Sugars)

n-Alkanoic acids (n=7)			Dicarboxylic acids (n=7)			Sugars (n=7)		
Compounds	Calibration curve Recovery (%)	MDL (ng/µL)	Compounds	Calibration curve Recovery (%)	MDL (ng/µL)	Compounds	Calibration curve Recovery (%)	MDL (ng/µL)
Octanoic acid, C8	102.77 ± 66.58	0.02	Malonic acid, C3	5.63 ± 3.18	0.328	D-(-)-Arabinose	56.00 ± 9.13	0.123
Nonanoic acid, C9	85.67 ± 40.29	0.024	Methylmalonic acid, iC4	28.74 ± 7.32	0.125	D-(-)-Ribose	203.02 ± 21.70	0.132
Decanoic acid, C10	90.37 ± 31.66	0.04	Maleic acid, M	58.50 ± 11.86	0.337	Levoglucosan	83.55 ± 9.37	0.122
Undecanoic acid, C11	111.72 ± 25.37	0.076	Succinic acid, C4	86.70 ± 6.47	0.118	D-(+)-Xylose	65.62 ± 5.95	0.077
Lauric acid, C12	112.28 ± 16.09	0.087	Methylsuccinic acid, iC5	86.07 ± 6.93	0.115	D-(-)-Fructose	39.98 ± 3.64	0.186
Tridecanoic acid, C13	104.60 ± 11.00	0.106	Methylmaleic acid, mM	68.25 ± 12.65	0.209	D-(+)-Mannose	51.22 ± 4.39	0.041
Myristic acid, C14	58.37 ± 28.12	0.089	Fumaric acid, F	73.08 ± 6.54	0.011	D-(+) Galactose	50.61 ± 4.30	0.058
Pentadecanoic acid, C15	57.24 ± 12.79	0.125	Glutaric acid, C5	98.35 ± 8.87	0.108	D-(+)-Glucose	82.04 ± 7.10	0.073
Palmitic acid, C16	102.50 ± 33.44	0.179	2-methylglutaric acid, iC6	96.56 ±8.45	0.189	Sucrose	11.39 ± 4.75	0.101
Heptadecanoic acid, C17	60.37 ± 27.97	0.107	D-Malic acid, hC4	35.85 ± 6.31	0.12	D-(+)-Maltose	5.75 ± 2.76	0.128
Stearic acid, C18	55.18 ± 35.98	0.093	Adipic acid, C6	93.87 ± 8.07	0.408			
Eicosanoic acid, C20	39.43 ± 31.66	0.085	Pimelic acid, C7	76.07 ± 6.51	0.297			
Heneicosanoic acid, C21	55.77 ± 34.95	0.217	Phthalic acid, Ph	50.84 ± 10.24	0.181			
Docosanoic acid, C22	16.35 ± 13.15	0.041	Suberic acid, C8	63.03 ± 6.68	0.27			
Tricosanoic acid, C23	3.36 ± 4.16	0.062	Iso-phthalic acid, iPh	60.53 ± 7.62	0.243			
Tetracosanoic acid, C24	0.01 ± 0.02	0.089	Tere-phthalic acid, TPh	54.69 ± 9.13	0.102			
Elaidic acid, *trans*-C18	67.33 ± 46.36	0.207	Azelaic acid, C9	45.18 ± 11.83	0.192			
			Sebacic acid, C10	112.58 ± 21.15	0.293			
			Undecanedionic acid, C11	33.86 ± 3.53	N.A			

N.A : Not Available. The MDL value for Undecanedionic acid, C11 was not identified in this study.

3.3 Results and discussions

3.3.1 Speciation results

Organic compounds speciation

A total of 77 targeted organic compounds were quantified using GC-MS (Agilent Technologies, 7890A, 5975C, USA) and the results of speciation are shown in Table 3-7 and Table 3-8. For the non-polar species, PAHs and n-Alkanes groups were determined while n-Alkanoic acid, Dicarboxylic acids, and Sugar groups represented the polar groups in this study. The overall concentration trends of organic compounds were very similar to that of $PM_{2.5}$ mass concentration in this study. The average concentration of organic compounds throughout the whole sampling period was 116.05 ± 66.19 ng m^{-3}, comprising 1.97% of the total OC in $PM_{2.5}$ (Fig. 3-2 (b)). The mass concentration is far lower than previous ambient particle studies in South Korea, for example, 393.44 ± 78.91 ng m^{-3} of $PM_{2.5}$ in Incheon during 2009 to 2010 (Choi et al. 2012) and 343 ± 27 ng m^{-3} of TSP in Gosan, Jeju Island during the springtime in 2005 (Wang, Kawamura, and Lee 2009). As shown in the supplementary Fig. S3-1, the monthly organic mass concentration was highest in May (244.36 ± 138.54 ng m^{-3}) and lowest in July (74.28 ± 25.71 ng m^{-3}). The average DCAs concentration accounted for more than half (total average of 78.75 ng m^{-3}, 67.86%) of the total organic compounds followed by n-Alkanoic acids (total average of 26.26 ng m^{-3}, 22.63%), n-Alkanes (total average of 10.02 ng m^{-3}, 8.63%), Sugars (total average of 0.54 ng m^{-3}, 0.47%), and PAHs (total average of 0.48 ng m^{-3}, 0.41%).

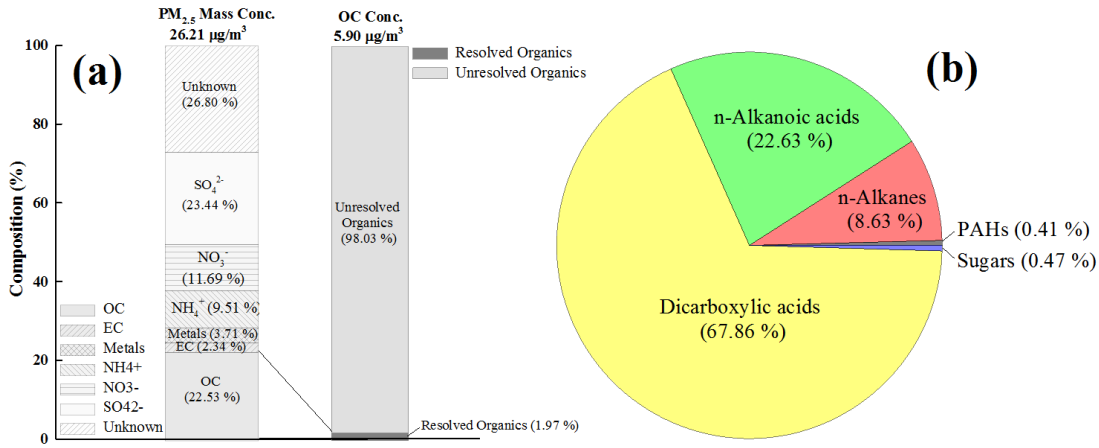

Fig. 3-2. Average contribution of each chemical species**.** (a) Chemical compositions of $PM_{2.5}$ and the ratio between unresolved organics and resolved organics (b) Contribution percentages of organic groups in a group of resolved organics

PAHs speciation

Polycyclic Aromatic Hydrocarbons (PAHs), which are semi-volatile, often originate from incomplete combustion or pyrolysis of organic compounds (Manoli, Kouras, and Samara 2004). The total number of 25 individual compounds were analyzed and the sum of total PAHs showed the smallest part of total organic compounds, which is less than 0.5%. For that reason, the seasonal concentration trend of PAHs seemed to have a weak influence on the average organic compounds concentration trends. Except for the case of May (0.49 ± 0.39 ng m^{-3}) where monthly $PM_{2.5}$ mass concentration was highest, the monthly concentration trend indicated the increasing concentration trend throughout June (0.28 ± 0.24 ng m^{-3}) to October (1.07 ± 0.50 ng m^{-3}). The trend of low PAHs concentrations in summer and high concentrations in winter seemed quite reasonable on the basis of former PAHs study results (Guo et al. 2003, Choi et al. 2012). The seasonal variations between summer and winter season

have been discovered that the lot of emission sources were originated from fossil fuel combustion, especially during the winter (Mazquiarán and de Pinedo 2007, Choi et al. 2012). Meanwhile, higher dispersion and photo-degradation effects contributed to lower concentration in summer season (Chang et al. 2006). Among individual PAHs compounds, benzo[b]fluoranthene, which has 4 rings showed the most abundant concentrations in this study. Though traditionally benzo[a]pyrene is used as a marker for PAHs, benzo[b]fluoranthene have been also suggested one of makers for PAHs (Straif et al. 2013).

The volatility of PAHs depends on the number of rings. PAHs with 3 or 4 rings (3-ring: phenanthrene and anthracene, 4-ring: fluoranthene, pyrene, benzo[a]anthracene, and chrysene) are classified as semi-volatile and existed in both gas phase and particulate phase while PAHs with 5 or 6 rings (5-ring : benzo[b]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene and benzo[e]pyrene, 6-ring : Indeno[1,2,3-cd]pyrene and benzo[ghi]perylene) are non-volatile PAHs only originate from solid phase particulates (Tan et al. 2011). The total average concentration of semi-volatile PAHs with 3 or 4 rings was 0.20 ± 0.18 ng m^{-3} and non-volatile PAHs with 5 or 6 rings was 0.27 ± 0.25 ng m^{-3}.

The method of BghiP/BeP, BeP/(BeP + BaP), Flt/(Flt+Pyr) and IcdP/(IcdP+BghiP) of PAHs were used as diagnostic ratios in this study. Note that the ratio of BghiP/BeP close to 2.0 refers source of gasoline while the value of 0.8 indicative of coal combustion (Ohura et al. 2004). BghiP/Bep value represented 0.20 in May and June, 0.69 in July, 1.00 in August, 0.95 in September, 0.66 in October in this study where the average BghiP/BeP ratio was 0.68. From this result, it was explained that PAHs sources in the sampling site were mainly influenced by coal combustion.

On the other hand, the BeP/(BeP + BaP) values were 0.77, 0.80, 0.85, 0.74, 0.79, and

0.76 in May, June, July, August, September, and October respectively. High values in June (0.80) and July (0.85) suggested a typical seasonal trend of summer since BaP is easy to decay with photo-oxidation processes (Wang et al. 2007). The average BeP/(BeP + BaP) value of 5.03 might refer the aging of particles because BeP and BaP concentration were similar in the environment when PAHs were from fresh emission sources (Jun Li et al. 2013).

The average ratio of Flt/(Flt+Pyr) was 0.56, which is classified as coal/biofuel emission (>0.5). The ratio lower than 0.4 is classified into petroleum and the ratio between 0.4-0.5 is determined as petroleum combustion sources from the previous works of literature (Liu et al. 2007, Gu et al. 2010, Tobiszewski and Namieśnik 2012).

The relative concentration of IcdP/(IcdP+BghiP) is also widely used as an indicator to distinguish petroleum combustion (<0.5) from coal combustion (>0.5) (Liu et al. 2007). Some literature suggested the value of 0.56 as the criteria of coal combustion (Grimmer et al. 1983, Pio, Alves, and Duarte 2001). The mean ratio of IcdP/(IcdP+BghiP) in May (0.74) and June (0.82) presented the value higher than 0.5. Meanwhile, other four months showed the ratio value below 0.5. The average ratio obtained in this study was 0.51, which might indicate the contribution of coal combustion around the sampling site.

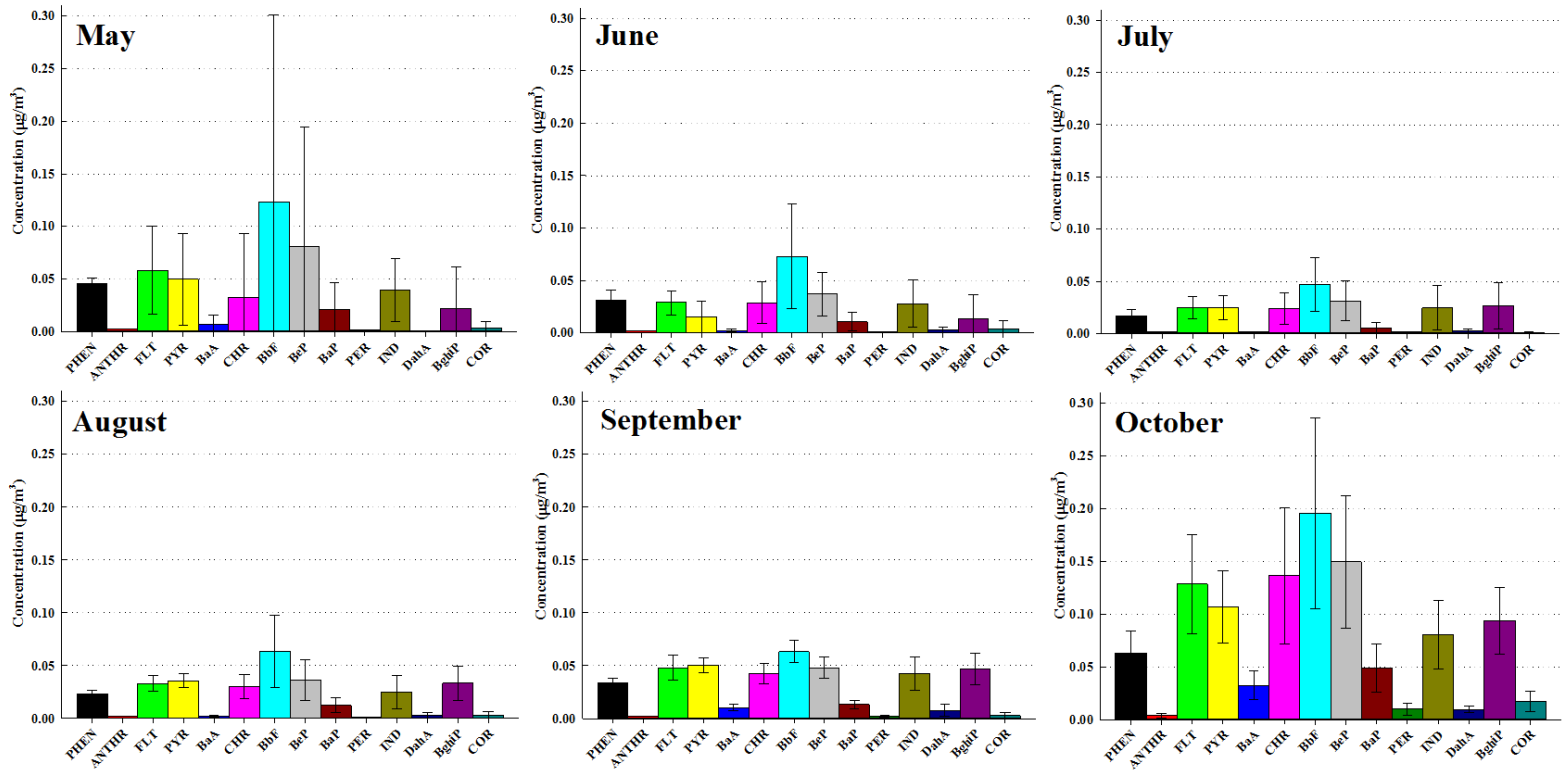

Fig. 3-3. Comparison of monthly individual PAHs concentrations (95% confidence interval)

n-Alkanes

n-Alkanes from C20 to C36 were analyzed in this study. Several studies have revealed that C21-C25 are indicators of diesel engine exhaust (Chellam, Kulkarni, and Fraser 2005). C27-C34 (especially higher odd n-alkanes such as C27, C29, C31 and C33) are known as makers of vegetable detritus (Simoneit 1989, Rogge, Hildemann, et al. 1993) The average n-Alkane concentration during the sampling period was 10.02 ± 7.46 ng m^{-3} varied from 1.29 ng m^{-3} to 28.93 ng m^{-3}. The portion of n-Alkanes in OC was about 8.6%, which was the third highest among organic groups. Compared to other two seasons (spring: 10.55 ± 8.61 ng m^{-3}, summer: 6.26 ± 4.81 ng m^{-3}), the monthly n-Alkanes trend represented high concentration during the autumn period (15.86 ± 7.39 ng m^{-3}). Hence, the seasonal pattern of high concentration during winter and low concentration during summer was well reflected in this study. Though there were no winter samples owing to the limited sampling period, seasonal distinctions between summer and autumn were identified. Fig.3-4 (a) shows the seasonal trend by carbon numbers of n-Alkanes. It was noticeable that C25, C27, C29, and C31 were highly peaked in every season and they are known as vegetable detritus markers. C27 shows the highest concentration throughout the whole sampling period (1.67 ± 1.70 ng m^{-3}). n-Alkanes with high carbon number (C33-C36) were excluded in CPI and WNA% calculation based on their inadequate recovery values.

Carbon Preference Index (CPI) is often used as an index for indicating the contribution of anthropogenic or biogenic sources. A CPI value close to or less than a value of 1 shows a likelihood of fossil fuel burning, while a value higher than 3 may indicate biological sources of fine particles in the atmosphere (Simoneit 1989). The CPI value for n-Alkanes was calculated based on the equation (3) below.

$$CPI_{n\text{-}alkane} = \frac{\Sigma \text{ Total odd number of carbons}}{\Sigma \text{ Total even number of carbons}} \quad (3)$$

Average n-Alkanes CPI value was determined as 2.33 ± 1.20, which shows the overall strong relationships with natural sources when compared to previous studies (Table 3-5). Unlike prior CPI studies in Incheon (1.44 to 1.55) and Seoul (1.17 to 2.60, 1.95 ± 0.82), which are metropolitan in Korea, this study showed relatively high CPI value over 2. The average CPI value from this study showed the largest value when compared to prior study cases from Table 3-5. This might reflect the characteristics of Daebu Island as a rural site with various natural sources. Seasonal difference of CPI between three seasons were found: spring (1.85 ± 0.77), summer (2.46 ± 1.48) and autumn (2.20 ± 0.67). Summer seemed to be the mostly affected season with non-anthropogenic sources along with the highest CPI value (8.26) in August 31 (Fig. 3-4).

C_{max} (maximum carbon number) is another well-known parameters of identifying source origins and maturity of aerosols. Highly matured aerosols from fossil fuels can only emit low value of C_{max} while high C_{max} comes from aerosols affected by plant wax sources (Duan, He, and Liu 2010). The C_{max} value in this study was C27 followed by C31 and C25. Most of the sampling months including May, June, September, and October showed the C_{max} of C27 except July and August. Instead, C21 was the C_{max} for July and the C_{max} of August was C31. Though July showed relatively low value in C_{max}, it is hard to say there was significant effects of fossil fuels since C31 and C29 were followed by C_{max} with not much difference in its concentration. The results from C_{max} well supported CPI of n-Alkanes in this study.

Quantifying the biogenic contribution with n-Alkanes assist in providing additional

information of environmental characteristics. The percentage of wax n-Alkanes (WNA%) is a useful tool for quantifying the contribution of biogenic sources in aerosols (Simoneit 1989). The equation for quantifying WNA% is expressed as below (4).

$$WNA\% = \frac{\Sigma\,[C_n - 0.5(C_{n+1} + C_{n-1})]}{\Sigma\ \text{n-Alkanes}} \times 100 \qquad (4)$$

When the C_n value is negative, the value is replaced with zero. The average WNA% during the whole period was 35.07 ± 12.50 ranged from 19.07 to 71.87. Highest WNA% was shown in August 31 along with the highest n-Alkane CPI value. The WNA% value in this study showed much higher contributions to plant wax composition in aerosols compare to previous studies (Table 3-6). Except the case study from India, the average WNA% value from present study were the highest. Daebu elementary school surrounded by green plants with small mountains, which are approximately 1.1 km from Ppeokkuksan Mountain (126°58'E, 37°26'N, 69.3 m) and 1.5 km from Hwanggeumsan Mountain (126°59'E, 37°25'N, 143.2 m) respectively. The high contribution of plant wax from forest region might be the important origins of such high WNA% in this study. The whole sampling period in this study was included in non-heating period (May-October) and this may contribute to the high value of WNA% coupled with high contributions in plant sources (Hu et al. 2013).

Table 3-5. C_{max} and CPI values from previous literatures

Location	Particle size	Sampling period	Cmax	CPI	Reference
Korea					
Daebu Island, Korea	$PM_{2.5}$	May 2016 to October 2016	C27, C31, C25	$CPI_{C20-C32}$:1.01-8.26, Average: 2.33 ± 1.20	Present study
Incheon, Korea	$PM_{2.5}$	June 2009 to May 2010	C25, C23, C28	CPI_{C9-C30}:1.44-1.55	Choi, Heo et al. 2012
Seoul, Korea	PM_{10}	April 2010 to April 2011	C27, C29, C31	$CPI_{C20-C34}$:1.17-2.60, Average: 1.95±0.82	Lee, Lim et al. 2015
Northeast Asia					
Guangzhou, China	TSP	April 2001 to July 2001	C20, C21, C22	$CPI_{C25-C35}$:0.77-1.18, Average: 0.98	Bi, Sheng et al. 2002
Tianjin, China	TSP	Nov 2003 to March 2003	C23, C22, C25	$CPI_{C12-C35}$:1.07-1.49	Wu, Tao et al. 2007
Qingdao, China	TSP	June 2001 to May 2002	C29, C23	$CPI_{C14-C36}$:1.17-5.20, Average: 1.93	Guo, Sheng et al. 2003
Beijing, China	$PM_{2.5}$	Sep 2003 to July 2004	C29, C21	$CPI_{C11-C34}$:1.18-3.88, Average: 1.18	Duan, He et al. 2010
Shanghai, China	$PM_{2.5}$	September 2009	C29	$CPI_{C17-C40}$:1.04-1.69, Average: 1.33	Cao, Zhu et al. 2013
Tokyo, Japan	TSP	April 1988 to February 1989	-	$CPI_{C17-C40}$:1.2-2.1	Yamamoto and Kawamura 2010
Taipei, Taiwan	$PM_{2.5}$	September 1997 to February 1998	C19, C24, C25	$CPI_{C17-C36}$:0.9-1.9	Young and Wang 2002
Other countries					
Selangor, Malaysia	$PM_{2.5}$	August 2011 to July 2012	C26, C27	$CPI_{C24-C32}$: 1.3 (southwestern monsoon), 1.9 (northeastern monsoon)	Fujii, Tohno et al. 2015
United Kingdom	TSP	June 1995 to July 1996	C25, C29	$CPI_{C19-C30}$: 1.28 (Bounds Green), 1.04 (St Paul's)	Kendall, Hamilton et al. 2001
Valencia, Spain	PM_{10}	September 2006 to October 2006	C30	$CPI_{C18-C30}$:0.8-1.3	Viana, López et al. 2008
Athens, Greece	$PM_{2.5}$	August 2003 to March 2004	C27	$CPI_{C14-C25}$:1.84	Andreou and Rapsomanikis 2009
California, USA	$PM_{2.5}$	February 2000 to January 2001	C31, C29	$CPI_{C17-C36}$:1.7	Rinehart, Fujita et al. 2006
Miami, USA	TSP	June 1994 to March 1995	C31, C29, C27	$CPI_{C25>}$:1.9	Lang, Zhang et al. 2002

Table 3-6. The percentage of wax n-Alkanes (WNA%) from previous studies and comparison with the present study result

Location	WNA%	References
Daebu Island, Korea	Average: 35.07 ± 12.50 41.15 ± 4.00 (May), 42.22 ± 11.91 (June), 19.12 ± 10.64 (July), 37.84 ± 15.82 (August), 35.95 ± 13.43 (September), 43.33 ± 9.53 (October)	Present study
Asia		
Shanghai, China	19 ± 1 (winter), 23 ± 2 (spring), 30 ± 3 (summer), 28 ± 2 (autumn)	Lyu, Xu et al. 2017
Nanjing, China	10.8 ± 10.6 to 15.6 ± 21.7	Wang, Huang et al. 2006
New Delhi, India	39 ± 10	Yadav, Tandon et al. 2013
Pahang, Malaysia	4.15 to 14.8	Tay, Yee et al. 2013
Other countries		
Prato, Italy	1.01	Cincinelli, Del Bubba et al. 2007
Eordea basin, Greece	20.6 ± 4.2 (Klitos), 35.8 ± 9.7 (Petrana)	Kalaitzoglou, Terzi et al. 2004
Elche, Spain	29	Chofre, Gil-Moltó et al. 2016

Table 3-7. Monthly non-polar species trends of $PM_{2.5}$

		Season						
		May (n=2)	June (n=7)	July (n=7)	August (n=8)	September (n=6)	October (n=8)	Average (n=38)
PAH species (ng m^{-3})	Phenanthrene (PHEN)	0.05	0.03	0.02	0.02	0.03	0.06	0.03
	Anthracene (ANTHR)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Fluoranthene (FLT)	0.06	0.03	0.03	0.03	0.05	0.13	0.05
	Pyrene (PYR)	0.05	0.02	0.02	0.04	0.05	0.11	0.05
	Benz[a]anthracene (BaA)	0.01	0.00	0.00	0.00	0.01	0.03	0.01
	Chrysene (CHR)	0.03	0.03	0.02	0.03	0.04	0.14	0.05
	Benzo[b]fluoranthene (BbF)	0.12	0.07	0.05	0.06	0.06	0.20	0.09
	Benzo[e]pyrene (BeP)	0.08	0.04	0.03	0.04	0.05	0.15	0.06
	Benzo[a]pyrene (BaP)	0.02	0.01	0.01	0.01	0.01	0.05	0.02
	Perylene (PER)	0.00	0.00	0.00	0.00	0.00	0.01	0.00
	Indeno[1,2,3-cd]pyrene (IND)	0.04	0.03	0.02	0.02	0.04	0.08	0.04
	Dibenz[a,h]anthracene (DahA)	0.00	0.00	0.00	0.00	0.01	0.01	0.01
	Benzo[ghi]perylene (BghiP)	0.02	0.01	0.03	0.03	0.05	0.09	0.04
	Coronene (COR)	0.00	0.00	0.00	0.00	0.00	0.02	0.01
	Σ PAHs	**0.49±0.39**	**0.28±0.24**	**0.24±0.17**	**0.30±0.17**	**0.41±0.08**	**1.07±0.50**	**0.48±0.42**
n-Alkane species (ng m^{-3})	Eicosane (C20)	1.96	0.05	0.04	0.07	0.06	0.07	0.16
	Heneicosane (C21)	0.24	0.36	0.50	0.71	0.46	0.16	0.43
	Docosane (C22)	0.10	0.09	0.07	0.32	0.07	0.24	0.16
	Tricosane (C23)	0.28	0.23	0.13	0.18	0.25	0.50	0.26
	Tetracosane (C24)	0.27	0.27	0.26	0.22	0.33	0.75	0.37
	Pentacosane (C25)	1.32	1.25	0.30	0.51	1.39	2.17	1.14
	Hexacosane (C26)	0.59	0.47	0.20	0.39	0.78	0.93	0.56
	Heptacosane (C27)	2.03	1.51	0.39	0.93	2.45	3.02	1.67
	Octacosane (C28)	0.36	0.27	0.19	0.34	0.68	0.75	0.44
	Nonacosane (C29)	1.10	0.74	0.44	0.92	1.35	1.76	1.05
	Triacontane (C30)	0.36	0.29	0.26	0.34	0.81	0.82	0.49
	Hentriacontane (C31)	0.95	0.97	0.44	1.24	1.45	2.76	1.38
	Dotriacontane (C32)	0.40	0.36	0.20	0.44	1.00	1.13	0.61
	Tritriacontane (C33)	0.53	0.53	0.34	0.64	1.73	1.94	1.01
	Tetratriacontane (C34)	0.01	0.04	0.01	0.01	0.42	0.44	0.17
	Pentatriacontane (C35)	0.02	0.02	0.01	0.04	0.07	0.08	0.04
	Hexatriacontane (C36)	0.05	0.06	0.01	0.02	0.16	0.16	0.08
	Σ n-Alkanes	**10.55±8.61**	**7.51±6.54**	**3.79±1.69**	**7.32±4.62**	**13.46±5.84**	**17.66±8.28**	**10.02±7.46**

n-Alkanoic acids

The second dominant organic compound of OC was n-Alkanoic acids (26.26 ng m^{-3}, 22.6%). The low molecular weight (< C20) compounds were known as the indicators of microorganisms (Simoneit and Mazurek 1982) while n-Alkanoic acids with high molecular weight (> C20) indicate Vascular plant wax sources. Some of those compounds, palmitic acids (C16) and steric acid (C18) are known as major constituents of seed oils utilized as cooking oils. Fuel combustion, meat cooking, microbial sources, and plant wax (Simoneit 1986, Rogge et al. 1991) were also distinguished by C16 and C18 markers in previous studies. In this study, the overall seasonal patterns were similar between different carbon numbers, where C16 and C 18 were markedly higher throughout the sampling period (Fig. 3-5). The average individual n-alkanoic acid concentration of C16 and C18 were 11.85 ± 3.71 ng m^{-3} and 7.71 ± 2.56 ng m^{-3}, respectively. According to previous studies, C16 and C18 were one of the most abundant species worldwide (Huang et al. 2006, Park et al. 2006, Choi et al. 2012). n-Alkanoic acids with odd numbers of carbons represent enriched (>1) naturally emitted hydrocarbons (Simoneit 1986).

$$CPI_{\text{n-alkanoic acids}} = \frac{\Sigma \text{ Total even number of carbons}}{\Sigma \text{ Total odd number of carbons}} \quad (5)$$

CPI values in this study were calculated using total even to odd for n-Alkanoic acids (C8-C18). The average CPI (C8-C18) value was 21.89 ± 8.93, showing a clear distribution of plant wax sources throughout the whole seasons. It was noticeable from the seasonal CPI plot (Fig.3-6) that the value was peaked during the late spring

(17.04 ± 4.50) to summer season (20.27 ± 9.29) while the values were decreased during autumn season (10.71 ± 2.10).

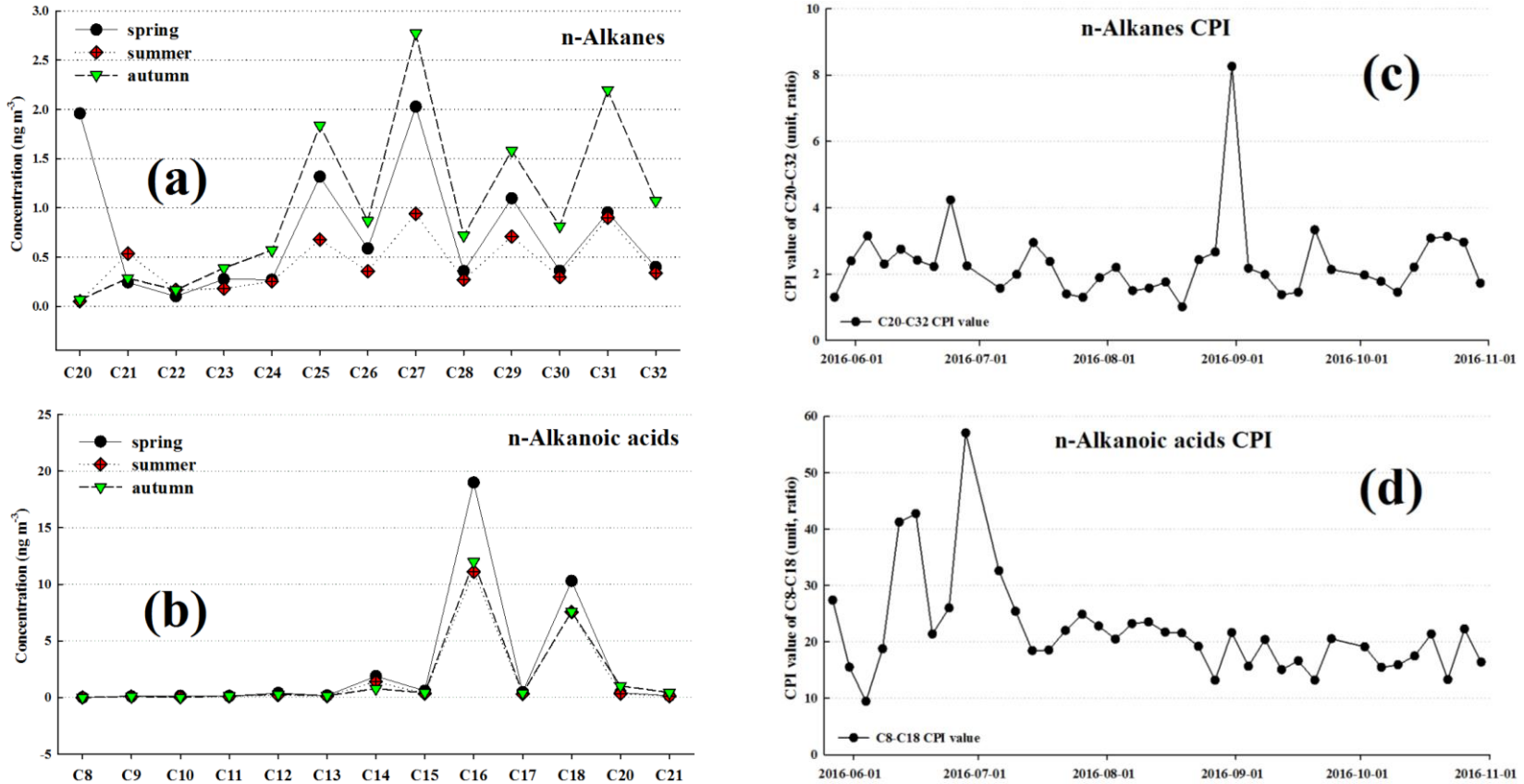

Fig. 3-4. Seasonal concentration trends and CPI values of n-Alkanes and n-Alkanoic acids during the sampling period in 2016

Dicarboxylic acids

Dicarboxylic acids (DCAs) are known as possible sources of photo-oxidations in the atmosphere and mostly exist in the particle phase owing to low vapor pressures (Li et al. 2006). Oxalic acid (C2), malonic acid (C3), and succinic acid (C4) are known as the most enrich species of DCAs in the urban atmosphere since the oxidants in the atmosphere react with unsaturated acids (Tsapakis et al. 2002, Sullivan and Prather 2007). A total 19 of DCAs compounds were targeted in this study: Saturated straight chain acids (malonic acid (C3), succinic acid (C4), glutaric acid (C5), adipic acid (C6), pimelic acid (C7), suberic acid (C8), azelaic acid (C9), sebacic acid (C10), undecanedionic acid (C11) and d-malic acid (hC4)), Unsaturated diacids (maleic acid (M), fumaric acids (F), methylmaleic acid (mM), phthalic acid (Ph), iso-phthalic acid (iPh) and tere-phthalic acid (TPh)), and Branched chain diacids (methylmalonic acid (iC4), methylsuccinic acid (iC5) and 2-methylglutaric acid (iC6)).

The average DCAs concentration of the total sampling period was 78.75 ± 57.12 ng m^{-3}, accounting for the largest portion (67.86%) of OC. While there are little differences in the seasonal concentration trend (high concentration in spring and low concentration in summer season) between individual DCAs, malonic acid (C3, 31.28 ± 27.86 ng m^{-3}), d-malic acid (hC4, 11.42 ± 12.09 ng m^{-3}) and tere-phthalic acid (TPh, 10.28 ± 6.99 ng m^{-3}) were the three most abundant components in the DCAs. Among saturated straight chain acids, the concentrations of short carbon chain DCAs (C3: 31.28 ± 27.86 ng m^{-3}, C4: 7.76 ± 12.15 ng m^{-3} and C5: 2.08 ± 3.05 ng m^{-3}) were relatively high and this concentration pattern showed consistent results with precedent studies (Yue and Fraser 2004, Huang et al. 2005, Park et al. 2006).

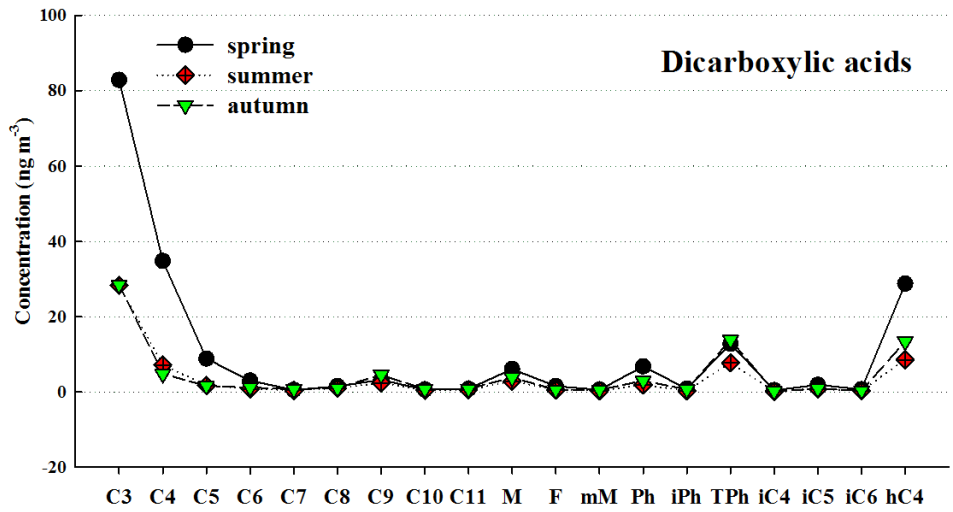

Fig. 3-5. Seasonal concentrations of different individual DCAs compounds

Sugars

A total of 10 sugar species were identified through organic analysis. The average concentration of sugar species was 0.54 ± 0.01 ng m^{-3}. The overall sugar concentration accounted for the small part of OC (0.47%) while levoglucosan (0.12 ± 0.00 ng m^{-3}) and sucrose (0.15 ± 0.00 ng m^{-3}) showed relatively high concentrations compared to other sugar compounds. Levoglucosan is a widely accepted fingerprint of biomass burning (Simoneit et al. 1999) and sucrose is a possible source of pollen, fungi, and spores (Feofilova et al. 2000, Pacini, Guarnieri, and Nepi 2006). Almost no seasonal difference was found except the very low concentration in July (0.01 ± 0.01 ng m^{-3}).

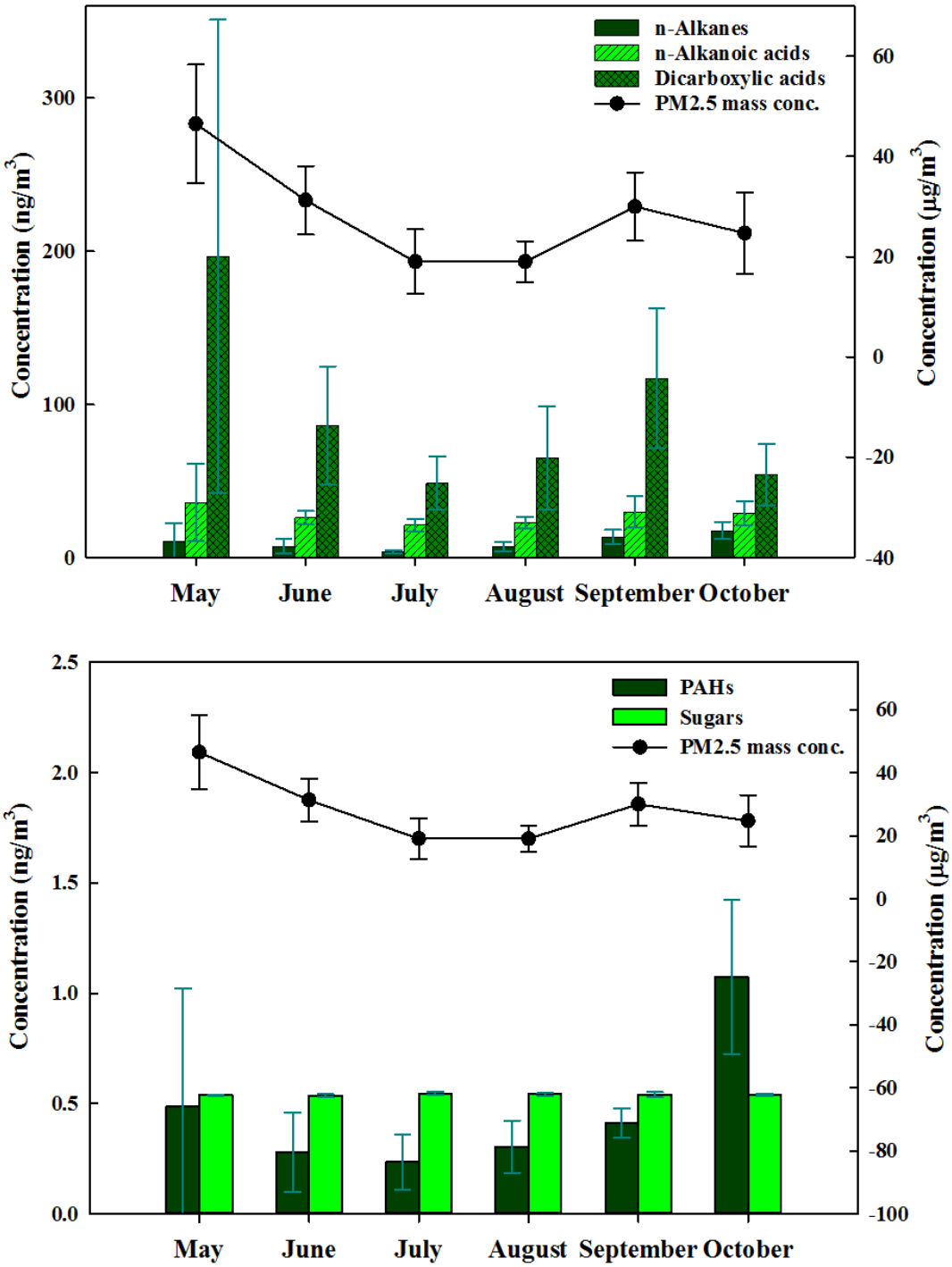

Fig. 3-6. Monthly concentration trends between five organic compounds groups

Table 3-8. Monthly polar species trends of $PM_{2.5}$

		Season						
		May (n=2)	June (n=7)	July (n=7)	August (n=8)	Septembe r (n=6)	October (n=8)	Average (n=38)
n-Alkanoic acid species (ng m^{-3})	Octanoic acid (C8)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Nonanoic acid (C9)	0.09	0.12	0.06	0.08	0.13	0.07	0.09
	Decanoic acid (C10)	0.14	0.06	0.05	0.06	0.01	0.01	0.04
	Undecanoic acid (C11)	0.12	0.15	0.06	0.08	0.11	0.16	0.11
	Lauric acid (C12)	0.40	0.27	0.15	0.19	0.25	0.32	0.24
	Tridecanoic acid (C13)	0.17	0.13	0.09	0.10	0.13	0.19	0.13
	Myristic acid (C14)	1.88	1.09	2.22	0.96	0.77	0.78	1.20
	Pentadecanoic acid (C15)	0.60	0.35	0.30	0.37	0.44	0.39	0.38
	Palmitic acid (C16)	19.00	12.16	9.97	11.19	11.30	12.50	11.85
	Heptadecanoic acid (C17)	0.47	0.29	0.29	0.34	0.37	0.40	0.35
	Stearic acid (C18)	10.30	9.25	6.51	6.98	7.66	7.54	7.71
	Eicosanoic acid (C20)	0.43	0.34	0.26	0.41	1.05	1.01	0.60
	Heneicosanoic acid (C21)	0.15	0.13	0.09	0.13	0.48	0.40	0.24
	Docosanoic acid (C22)	0.74	0.49	0.31	0.55	2.53	1.80	1.08
	Tricosanoic acid (C23)	0.33	0.24	0.17	0.25	1.05	0.96	0.51
	Tetracosanoic acid (C24)	1.12	0.72	0.45	0.80	3.35	2.38	1.47
	Elaidic acid (*trans*-C18)	0.13	0.19	0.28	0.44	0.22	0.15	0.25
	Σ n-Alkanoic acids	**36.07± 18.19**	**25.99± 5.84**	**21.26± 5.48**	**22.93± 5.18**	**29.85± 12.86**	**29.05± 11.07**	**26.26± 9.28**
DCAs species (ng m^{-3})	Malonic acid (C3)	82.87	39.27	17.85	27.99	50.81	11.80	31.28
	Methylmalonic acid (iC4)	0.46	0.31	0.09	0.14	0.26	0.13	0.19
	Maleic acid (M)	6.06	3.63	2.27	2.71	3.60	3.94	3.37
	Succinic acid (C4)	34.80	15.55	3.18	3.38	7.69	2.61	7.76
	Methylsuccinic acid (iC5)	1.89	1.17	0.52	0.58	0.92	0.82	0.85
	Methylmaleic acid (mM)	0.58	0.40	0.29	0.37	0.52	0.55	0.43
	Fumaric acid (F)	1.56	0.57	0.30	0.62	0.83	0.45	0.60
	Glutaric acid (C5)	8.83	3.17	0.95	1.20	2.45	1.02	2.08
	2-methylglutaric acid (iC6)	0.72	0.39	0.24	0.29	0.44	0.32	0.35
	D-Malic acid (hC4)	28.78	8.98	5.86	10.60	22.83	6.33	11.42
	Adipic acid (C6)	3.00	1.05	0.61	0.90	1.72	0.81	1.10
	Pimelic acid (C7)	0.54	0.47	0.35	0.50	0.85	0.63	0.55
	Phthalic acid (Ph)	6.78	1.92	1.83	1.84	3.20	2.84	2.54
	Suberic acid (C8)	1.53	0.88	0.80	1.23	1.20	0.94	1.04
	Iso-phthalic acid (iPh)	0.85	0.31	0.27	0.30	0.58	0.68	0.45
	Tere-phthalic acid (TPh)	12.82	5.24	10.18	7.88	13.33	14.27	10.28
	Azelaic acid (C9)	3.22	2.01	1.95	3.22	4.31	4.73	3.25
	Sebacic acid (C10)	0.61	0.32	0.38	0.56	0.68	0.73	0.54
	Undecanedionic acid (C11)	0.81	0.50	0.51	0.69	0.81	0.79	0.67
	Σ Dicarboxylic acids	**196.72± 111.36**	**86.13± 52.32**	**48.45± 23.35**	**64.99± 48.89**	**117.03± 57.05**	**54.38± 29.07**	**78.75± 57.12**
Sugar species (ng m^{-3})	D-(-)-Arabinose	0.02	0.02	0.00	0.02	0.02	0.02	0.02
	D-(-)-Ribose	0.02	0.02	0.00	0.02	0.02	0.02	0.02
	Levoglucosan	0.12	0.12	0.00	0.13	0.12	0.12	0.12
	D-(+)-Xylose	0.01	0.01	0.00	0.01	0.01	0.01	0.01
	D-(-)-Fructose	0.07	0.07	0.00	0.07	0.07	0.07	0.07
	D-(+)-Mannose	0.01	0.01	0.00	0.01	0.01	0.01	0.01
	D-(+) Galactose	0.07	0.07	0.00	0.07	0.07	0.07	0.07
	D-(+)-Glucose	0.04	0.04	0.00	0.05	0.05	0.04	0.04
	Sucrose	0.15	0.15	0.00	0.15	0.15	0.15	0.15
	D-(+)-Maltose	0.02	0.02	0.00	0.02	0.02	0.02	0.02
	Σ Sugars	**0.54± 0.00**	**0.54± 0.01**	**0.01± 0.01**	**0.54± 0.01**	**0.54± 0.01**	**0.54± 0.01**	**0.54± 0.01**

Table 3-9. Monthly trends of $PM_{2.5}$ organic and inorganic constituents in Daebu Island, Korea

		Season						
		May	June	July	August	September	October	Average
Elemental Species ($\mu g\ m^{-3}$)	$PM_{2.5}$	46.50±14.74	31.26±13.53	19.00±12.73	19.02±8.05	30.00±12.55	24.70±14.93	26.21±14.50
	OC	8.63±3.72	5.23±2.23	3.85±2.32	5.71±4.73	6.76±3.24	7.23±3.47	5.90±3.52
	EC	0.53±0.13	0.36±0.12	0.43±0.13	0.59±0.13	0.76±0.23	0.99±0.32	0.61±0.29
	NO_3^-	7.43±4.85	5.23±2.81	1.51±1.24	0.91±0.72	1.27±1.87	4.77±5.15	3.06±3.61
	SO_4^{2-}	9.56±4.28	9.13±4.02	5.66±3.93	7.05±3.58	3.11±4.39	4.38±4.25	6.14±4.52
	NH_4^+	6.34±2.81	5.24±2.35	1.91±1.55	1.43±1.06	0.89±1.37	1.44±1.91	2.49±2.56
	OC/EC	15.76±4.19	14.28±2.81	8.65±3.17	9.46±7.95	8.82±2.95	7.32±2.63	10.14±5.12
	WSOC	4.70±2.64	4.74±2.24	2.12±1.85	1.63±1.26	3.35±2.01	2.99±2.40	3.07±2.28
	WIOC	3.93±1.81	0.95±1.20	1.75±0.98	4.08±4.68	3.44±2.19	4.24±1.43	2.95±2.73
	POC	2.47±0.53	1.76±0.51	2.03±0.53	2.70±0.54	3.41±0.96	4.39±1.35	2.80±1.21
	SOC	6.16±3.30	3.47±1.81	1.82±1.90	3.01±4.58	3.35±2.69	2.88±2.95	3.15±3.07
	Σ Soil[a]	1.04±0.38	0.57±0.27	0.31±0.17	0.50±0.32	0.57±0.36	0.92±0.56	0.60±0.42
	Σ Toxic metals[b]	0.23±0.13	0.41±0.74	0.14±0.14	0.13±0.13	0.17±0.26	0.12±0.10	0.20±0.36
Organic Species ($ng\ m^{-3}$)	Levoglucosan	0.12±0.00	0.12±0.00	0.13±0.00	0.13±0.00	0.12±0.00	0.12±0.00	0.12±0.00
	Σ PAHs	0.49±0.39	0.28±0.24	0.24±0.17	0.30±0.17	0.41±0.08	1.07±0.50	0.48±0.42
	Σ n-Alkanes	10.55±8.61	7.51±6.54	3.79±1.69	7.32±4.62	13.46±5.84	17.66±8.28	10.02±7.46
	Σ n-Alkanoic acids	36.07±18.19	25.99±5.84	21.26±5.48	22.93±5.18	29.85±12.86	29.05±11.07	26.26±9.28
	Σ Dicarboxylic acid	196.72±111.36	86.13±52.32	48.45±23.35	64.99±48.89	117.03±57.05	54.38±29.07	78.75±57.12
	Σ Sugars	0.41±0.00	0.41±0.01	0.42±0.01	0.42±0.01	0.42±0.01	0.42±0.01	0.42±0.01

[a] Soil : Mg, Al, K, Ca, Mn and Fe

[b] Toxic metals : Cr, Cu, Ni, Pb, Dd, V, Sr, As, Se, Zn and Co

3.3.2 Principal Component Analysis (PCA) Results

Source apportionment of $PM_{2.5}$ using principal component analysis (PCA) was performed using $PM_{2.5}$ chemical species and organic compounds analysis data sets. The PCA analysis has been widely used in scientific fields as an effective tool for describing inter-correlated variables (Abdi and Williams 2010) into independent principal components (PCs) based on the orthogonal rotation called VARIMAX. PCA identified six factors using statistical software (SPSS ver. 22.0), which are Secondary Organic Aerosols 1 (SOAs 1), Combustion related sources, Secondary Organic Aerosols 2 (SOAs 2), Secondary inorganic factor, Biomass burning, and Industrial sources were estimated to possible sources of $PM_{2.5}$ in Daebu Island (Table 3-1). The six factors above the eigenvalue of 1 were extracted as reasonable principal components (PCs) that can well describe the analysis results. High factor loading values greater than 0.600 were highlighted in bold text to allow easy recognition of high correlations while the values below zero were eliminated in the table. A total sum of variance (%) was 86.651% and constituents the top two factors explained more than half of the total variances.

The PCA analysis with the dicarboxylic acid group was initially performed before applying PCA with inorganic and organic $PM_{2.5}$ component to extract individual compounds that can well explain the characteristics of DCAs. Supplementary table S3-2 explains the results from PCA results of DCAs and the first factor was considered as the representative of a DCAs group in this study.

The sources of dicarboxylic acids can be both anthropogenic and biogenic but it is obvious that they are good indicators of secondary aerosols (Ray and McDow 2005). Maleic acid is known to comes from anthropogenic gaseous hydrocarbons and Phthalic acid possibly originate from the oxidation process of PAHs (i.e. naphthalene)

(Kawamura and Ikushima 1993) as well as combustion sources. Photo-chemical reaction of cyclohexene may produce Adipic acid and Succinic acid concentration was high in the environment where there were lots of automobile emissions (Kawamura and Kaplan 1987). Glutaric acid is often identified as a constituents of secondary organic aerosol in the atmosphere (Baustian, Wise, and Tolbert 2010).

Factor 1 accounted for the largest part of the total variance (38.568%) with the eigenvalue of 9.256. High loadings with WSOC and individual dicarboxylic acids compounds characterized this factor as Secondary Organic Aerosols 1 (SOAs 1). Dicarboxylic acids which are known as products from photo-oxidation process are well identified as precursors of secondary aerosols and they are major components that largely contribute to Water-Soluble Organic Carbons (WSOC) (Simoneit et al. 2004, Ho et al. 2007) and thereby it seemed reasonable to define the factor 1 as a Secondary Organic Aerosols 1 (SOAs 1).

Factor 2, which showed the second highest variance (20.170%) was classified as Combustion related sources. Combustion related sources along with predominant values in EC, POC, Soil, ΣPAHs, and Σn-Alkanes among $PM_{2.5}$ chemical speciation data. Elemental Carbon (EC) originated from incomplete combustion process of carbonaceous matters (Feng et al. 2009) as well as Polycyclic Aromatic Hydrocarbons (PAHs) are produced during the incomplete combustions and the majority of the compounds are from anthropogenic sources (Venkataraman, Lyons, and Friedlander 1994). Not every element of n-Alkane compounds are from combustion sources but Chellam et al., (2005) describes that low carbon n-Alkanes including n-henicosane (C21), n-docosane (C22), n-tricosane (C23), n-tetracosane (C24), and n-pentacosane (C25) might be the possible indicator of disel engine exhaust. Those loadings in factor 2 described the feature as a combustion related

sources with the eigenvalue of 4.841.

Factor 3 was responsible for 2.446% of the total variance and the characteristics as Secondary Organic Aerosols 2 (SOAs 2) were distinguished by high loadings with OC, WIOC, and SOC. Though the concept that most of the Secondary Organic Aerosols (SOAs) are characterized as water-soluble due to photo-oxidation procedures has been pervasive in many studies, some study cases verified that significant contributions of water insoluble species to secondary organic carbons (Favez et al. 2008, Sciare et al. 2011). In a literature from Sciare et al., 2011, approximately 85% of the organic matter in residual organic source has water-insoluble characteristics while it discovered that contributions of semi-volatile primary combustion emissions from fossil fuels could be hardly oxidized and therefore have characteristics of water-insoluble characteristics. Another study case done in a semi-arid urban environment (Cairo, Egypt), demonstrated that the anthropogenic VOCs may contribute to the formation of SOA with low hydrophilicity (Favez et al. 2008) and the study also indicated that most of primary emissions from fossil fuel combustions are made up of water-insoluble materials. Fig. 3-1 supports the assumptions with the increasing trend of POC and WIOC between June and October. This result may indicate that $PM_{2.5}$ in Daebu Island was highly affected by anthropogenic and combustion sources.

In the case of factor 4, the most predominant values in SO_4^{2-} and NH_4^+ represent the feature of the secondary inorganic factor with the variance of 7.464%. The high correlation between SO_4^{2-} and NH_4^+ (0.853) indicate the most of the sulfate compounds were existed in a form of $(NH_4)_2SO_4$ (ammonium sulfate) (Contini et al. 2010).

Factor 5 contributed the 5.833% of the total variance. Strong loadings with

Levoglucosan and Sugar (0.980) suggested the possibility as biomass burning sources whereas other speciation elements showed relatively low correlations with the factor 5. Levoglucosan, the most important fingerprint of biomass burning, is not easily degradable in the atmosphere even with sunlight (Locker 1988) and therefore even remain stable for long-range transport from remote areas (Fraser and Lakshmanan 2000).

The sixth factor was highly related to toxic metal compounds which were distinguished as industrial sources. It accounted for 4.455% of the total variance. The factor of Toxic metals was the sum of Cu, Ni, Pb, Cd, V, Sr, As, Se, Zn, and Co in this analysis.

Table 3-10. Correlation coefficient matrix of $PM_{2.5}$ species

	OC	EC	WSOC	WIOC	POC	SOC	NO_3^-	SO_4^{2-}	NH_4^+	Soil	Toxic metals	LEVO	Σ PAHs	Σ Alkanes	Σ Alkanoic acids	Σ DCAs	Σ Sugars
OC	1	**0.426**	0.29	**0.871**	**0.426**	0.919	0.147	-	0.013	**0.427**	0.14	0.054	0.396	**0.502**	**0.55**	0.34	0.054
EC		1	0.056	**0.406**	1	0.036	0.163	-	-	**0.452**	0.173	-	0.57	**0.706**	0.36	0.128	-
WSOC			1	-	0.056	0.296	**0.441**	0.295	**0.486**	**0.451**	0.296	-	0.174	0.385	**0.625**	**0.638**	-
WIOC				1	**0.406**	**0.786**	-	-	-	0.204	-	0.169	0.314	0.314	0.24	0.019	0.169
POC					1	0.036	0.163	-	-	**0.452**	0.173	-	0.57	**0.706**	0.36	0.128	-
SOC						1	0.091	0.165	0.176	0.275	0.079	0.078	0.189	0.248	**0.451**	0.32	0.078
NO_3^-							1	0.349	**0.635**	**0.409**	0.225	-	0.093	0.229	0.396	0.396	-
SO_4^{2-}								1	**0.853**	0.052	-	0.058	-	-	0.027	0.26	0.058
NH_4^+									1	0.142	0.102	-	-	-	0.189	0.445	-
Soil										1	0.332	0.097	**0.719**	**0.653**	**0.522**	0.385	0.097
Toxic metals											1	-	0.026	0.143	-	0.371	-
LEVO												1	0.063	-	-	-	1
Σ PAHs													1	**0.711**	0.327	0.011	0.063
Σ Alkanes														1	**0.696**	0.294	-
Σ Alkanoic acid															1	**0.543**	-
Σ DCAs																1	-
Σ Sugars																	1

*Correlation value less than 0 were excluded and the value above 0.4 was shown in bold

Table 3-11. PCA analysis of $PM_{2.5}$ with factor loading results

		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communalities
	Identified sources	Secondary Organic Aerosols 1 (SOAs1)	Combustion related sources	Secondary Organic Aerosols 2 (SOAs2)	Secondary inorganic factor	Biomass burning	Industrial sources	
$PM_{2.5}$ Chemical Speciation	OC	.189	.364	**.905**	.029	.011	.036	.990
	EC	-	**.837**	.121	-	-	.173	.836
	WSOC	**.634**	.261	.043	.416	-	-	.696
	WIOC	-	.237	**.901**	-	.127	.039	.937
	POC	-	**.837**	.121	-	-	.173	.836
	SOC	.214	.038	**.947**	.161	.033	-	.973
	NO_3^-	.563	.259	-	.451	.069	.161	.628
	SO_4^{2-}	.102	-	.059	**.885**	.047	-	.873
	NH_4^+	.456	-	-	**.818**	.012	.030	.923
	Soil	.276	**.754**	.118	.289	.142	.154	.787
	Toxic metals	.229	.128	.035	.040	-	**.907**	.903
Organic Compounds Speciation	Levoglucosan	-	.006	.067	.023	**.980**	-	.981
	Σ PAHs	-	**.822**	.116	-	.081	-	.706
	Σ n-Alkanes	.237	**.857**	.181	-	-	-	.847
	Σ n-Alkanoic acids	.498	.528	.314	.157	-	-	.770
	Methylmalonic acid	**.828**	-	.096	.286	-	.189	.838
	Maleic acid	**.800**	.389	.074	.141	-	.059	.836
	Succinic acid	**.932**	-	-	.172	-	.121	.940
	Methylsuccinic acid	**.926**	.073	.001	.244	.001	.053	.925
	Glutaric acid	**.954**	-	-	.019	-	.080	.929
	2-methylglutaric acid	**.950**	.130	.131	.054	.016	-	.942
	Adipic acid	**.933**	.075	.109	-	-	.031	.919
	phthalic acid	**.806**	.313	.182	.112	-	-	.799
	Σ Sugars	-	.006	.067	.023	**.980**	-	.981
	Eigenvalues	9.256	4.841	2.446	1.784	1.400	1.069	
	Variance (%)	38.568	20.170	10.191	7.434	5.833	4.455	
	Cumulative (%)	38.568	58.738	68.929	76.363	82.196	86.651	

3.4 Conclusions

Chemical characteristics of $PM_{2.5}$ with organic compounds were investigated in Daebu Island, Korea. Samples were gathered every four-day from May 27 to October 30 in 2016. Carbonaceous characteristics of $PM_{2.5}$ were determined with WSOC, POC, SOC and WIOC concentration. The chemical speciation results of both $PM_{2.5}$ inorganic compounds and organic compounds were applied to PCA. Below is the summary of conclusions from this study.

(1) The average Water Soluble Organic Carbon (WSOC) concentration was 3.06 ± 2.28 μg m^{-3}, accounting for more than half of the total Organic Carbon (OC) concentration. WSOC/OC ratio peaked during the summer time and this indicated the elevation of secondary organic aerosols even though the low concentration of SOC and WSOC were observed in July. Unlike SOC and WSOC, Primary Organic Carbon (POC) and Water Insoluble Organic Carbon (WIOC) peaked in October.

(2) A total sum of individual organic compounds was highest in May while lowest in July, which were 244.36 ± 138.54 ng m^{-3} and 74.28 ± 25.71 ng m^{-3}, respectively. Dicarboxylic acids (DCAs), usually originate from photo-oxidation process, contributed the most of the organic compounds (78.75 ng m^{-3}, 67.86%). Other four organic group constitutes relatively small part of resolved-organic compounds followed by n-Alkanoic acids (26.26 ng m^{-3}, 22.63%), n-Alkanes (10.02 ng m^{-3}, 8.63%), Sugars (0.54 ng m^{-3}, 0.47%) and PAHs (0.48 ng m^{-3}, 0.41%).

(3) PAHs diagnostic ratios suggested the high possibility of anthropogenic combustion sources around the sampling site. Average CPI value of n-Alkanes was 2.33 ± 1.20 showing the strong relationship with natural sources. Moreover, n-

Alkanoic acids CPI value also indicated the presence of plant wax across whole sampling seasons. The percentage of wax n-Alkanes (WNA%) with high value (35.07 ± 12.50) clarified the sampling site was highly affected by plant sources.

(4) Six factors of $PM_{2.5}$ were identified by PCA. Secondary Organic Aerosols 1 (SOAs 1) (38.568%) and Combustion related sources (20.170%) accounted for more than half of the total variance (%), holding a majority of total concentrations. Secondary Organic Aerosols 2 (SOAs 2) (10.191%), Secondary inorganic factor (7.434%), Biomass burning (5.833%), and Industrial sources (4.455%) were other four factors, comprising about 28% of the total. PCA results indicated a large amount of $PM_{2.5}$ in Daebu Island was originated from both secondary aerosols and combustion sources.

(5) The Water-Insoluble Organic Carbon (WIOC) and Secondary Organic Carbon (SOC) were grouped in the same factor in PCA analysis which may indicate the potential anthropogenic VOCs.

The organic analysis of $PM_{2.5}$ in the sampling site also showed mixed source characteristics with high contributions of secondary aerosols. Further study for identifying the region of each source origin is expected in the future to effective control of anthropogenic sources around the sampling site.

References

Yeongheung Division [cited June 17, 2017. Available from http://www.kosep.co.kr:8100/kosep/hw/en/ov/ovhw18/main.do?menuCd=EN02030102&search=YEONGHEUNG.

Aas, Wenche, and Knut Breivik. 2005. *Heavy Metals and POP Measurements, 2003*: Norwegian Institute for Air Research.

Abdi, Hervé, and Lynne J Williams. 2010. "Principal component analysis." *Wiley interdisciplinary reviews: computational statistics* no. 2 (4):433-459.

Ackerman, Andrew S, Michael P Kirkpatrick, David E Stevens, and Owen B Toon. 2004. "The impact of humidity above stratiform clouds on indirect aerosol climate forcing." *Nature* no. 432 (7020):1014-1017.

Ades, AE, and G Kazantzis. 1988. "Lung cancer in a non-ferrous smelter: the role of cadmium." *British journal of industrial medicine* no. 45 (7):435-442.

Alexis, A, P Cox, A Lin, C Nguyen, and M Nystrom. 2005. "The California almanac of emissions and air quality." *California Air Resources Board, CA*.

Almeida, SM, CA Pio, MC Freitas, MA Reis, and MA Trancoso. 2006. "Approaching PM 2.5 and PM 2.5− 10 source apportionment by mass balance analysis, principal component analysis and particle size distribution." *Science of the Total Environment* no. 368 (2):663-674.

Andreae, Meinrat O. 1983. "Soot carbon and excess fine potassium: Long-range transport of combustion-derived aerosols." *Science* no. 220 (4602):1148-1151.

Ashbaugh, Lowell L, William C Malm, and Willy Z Sadeh. 1985. "A residence time probability analysis of sulfur concentrations at Grand Canyon National Park." *Atmospheric Environment (1967)* no. 19 (8):1263-1270.

Baustian, KJ, ME Wise, and MA Tolbert. 2010. "Depositional ice nucleation on solid ammonium sulfate and glutaric acid particles." *Atmospheric Chemistry and Physics* no. 10 (5):2307-2317.

Bell, Michelle L, Keita Ebisu, Brian P Leaderer, Janneane F Gent, Hyung Joo Lee, Petros Koutrakis, Yun Wang, Francesca Dominici, and Roger D Peng. 2014. "Associations of PM2. 5 Constituents and Sources with Hospital Admissions: Analysis of Four Counties in Connecticut and Massachusetts (USA) for Persons> or= 65 Years of Age." *Environmental Health Perspectives (Online)* no. 122 (2):138.

Biggins, Peter DE, and Roy M Harrison. 1979. "Characterization and classification of atmospheric sulfates." *Journal of the Air Pollution Control Association*

no. 29 (8):838-840.

Cabada, Juan C, Spyros N Pandis, Ramachandran Subramanian, Allen L Robinson, Andrea Polidori, and Barbara Turpin. 2004. "Estimating the secondary organic aerosol contribution to PM2. 5 using the EC tracer method special issue of aerosol science and technology on findings from the fine particulate matter supersites program." *Aerosol Science and Technology* no. 38 (S1):140-155.

Calloway, CP, S Li, JW Buchanan, and RK Stevens. 1989. "A refinement of the potassium tracer method for residential wood smoke." *Atmospheric Environment (1967)* no. 23 (1):67-69.

Cass, Glen R. 1998. "Organic molecular tracers for particulate air pollution sources." *TrAC Trends in Analytical Chemistry* no. 17 (6):356-366.

Chan, YC, RW Simpson, GH Mctainsh, PD Vowles, DD Cohen, and GM Bailey. 1999. "Source apportionment of PM 2.5 and PM 10 aerosols in Brisbane (Australia) by receptor modelling." *Atmospheric Environment* no. 33 (19):3251-3268.

Chang, Kuan-Foo, Guor-Cheng Fang, Jhy-Cherng Chen, and Yuh-Shen Wu. 2006. "Atmospheric polycyclic aromatic hydrocarbons (PAHs) in Asia: a review from 1999 to 2004." *Environmental pollution* no. 142 (3):388-396.

Charron, Aurelie, and Roy M Harrison. 2003. "Primary particle formation from vehicle emissions during exhaust dilution in the roadside atmosphere." *Atmospheric Environment* no. 37 (29):4109-4119.

Chellam, Shankararaman, Pranav Kulkarni, and Matthew P Fraser. 2005. "Emissions of organic compounds and trace metals in fine particulate matter from motor vehicles: a tunnel study in Houston, Texas." *Journal of the Air & Waste Management Association* no. 55 (1):60-72.

Choi, Jong-Kyu, Jong-Bae Heo, Soo-Jin Ban, Seung-Muk Yi, and Kyung-Duk Zoh. 2012. "Chemical characteristics of PM 2.5 aerosol in Incheon, Korea." *Atmospheric environment* no. 60:583-592.

Choi, Jong-kyu, Jong-Bae Heo, Soo-Jin Ban, Seung-Muk Yi, and Kyung-Duk Zoh. 2013. "Source apportionment of PM 2.5 at the coastal area in Korea." *Science of the Total Environment* no. 447:370-380.

Chow, Judith C, John G Watson, Eric M Fujita, Zhiqiang Lu, Douglas R Lawson, and Lowell L Ashbaugh. 1994. "Temporal and spatial variations of PM2. 5 and PM10 aerosol in the Southern California air quality study." *Atmospheric Environment* no. 28 (12):2061-2080.

Chu, Shao-Hang. 2005. "Stable estimate of primary OC/EC ratios in the EC tracer method." *Atmospheric Environment* no. 39 (8):1383-1392.

Cohen, David D, Jagoda Crawford, Eduard Stelcer, and Vuong Thu Bac. 2010. "Characterisation and source apportionment of fine particulate sources at Hanoi from 2001 to 2008." *Atmospheric Environment* no. 44 (3):320-328.

Cohen, David D, Jarrod W Martin, and Graham M Bailey. 1993. "The determination of fine particle sulfur levels in the Wollongong, Newcastle and Sydney areas." *Clean Air: Journal of the Clean Air Society of Australia and New Zealand* no. 27 (2):63.

Contini, D, A Genga, D Cesari, M Siciliano, A Donateo, MC Bove, and MR Guascito. 2010. "Characterisation and source apportionment of PM10 in an urban background site in Lecce." *Atmospheric Research* no. 95 (1):40-54.

Cornbleet, P Joanne, and Nathan Gochman. 1979. "Incorrect least-squares regression coefficients in method-comparison analysis." *Clinical chemistry* no. 25 (3):432-438.

Coulibaly, Souleymane, Hiroki Minami, Maho Abe, Tomohiro Hasei, Nobuyuki Sera, Shigekazu Yamamoto, Kunihiro Funasaka, Daichi Asakawa, Masanari Watanabe, and Naoko Honda. 2015. "Seasonal fluctuations in air pollution in Dazaifu, Japan, and effect of long-range transport from mainland East Asia." *Biological and Pharmaceutical Bulletin* no. 38 (9):1395-1403.

Duan, Fengkui, Kebin He, and Xiande Liu. 2010. "Characteristics and source identification of fine particulate n-alkanes in Beijing, China." *Journal of Environmental Sciences* no. 22 (7):998-1005.

Favez, Olivier, Jean Sciare, Hélène Cachier, Stéphane C Alfaro, and Magdy M Abdelwahab. 2008. "Significant formation of water-insoluble secondary organic aerosols in semi-arid urban environment." *Geophysical Research Letters* no. 35 (15).

Feng, Yanli, Yingjun Chen, Hui Guo, Guorui Zhi, Shengchun Xiong, Jun Li, Guoying Sheng, and Jiamo Fu. 2009. "Characteristics of organic and elemental carbon in PM 2.5 samples in Shanghai, China." *Atmospheric Research* no. 92 (4):434-442.

Feofilova, EP, VM Tereshina, NS Khokhlova, and AS Memorskaya. 2000. "Different mechanisms of the biochemical adaptation of mycelial fungi to temperature stress: changes in the cytosol carbohydrate composition." *Microbiology* no. 69 (5):504-508.

Fischer, AB, R Georgieva, V Nikolova, J Halkova, A Bainova, V Hristeva, D Penkov, and D Alandjiisk. 2003. "Health risk for children from lead and cadmium near a non-ferrous smelter in Bulgaria." *International journal of hygiene and environmental health* no. 206 (1):25-38.

Fraser, Matthew P, and Kalyan Lakshmanan. 2000. "Using levoglucosan as a molecular marker for the long-range transport of biomass combustion

aerosols." *Environmental Science & Technology* no. 34 (21):4560-4564.

Gelencsér, András, Barbara May, David Simpson, Asunción Sánchez-Ochoa, Anne Kasper-Giebl, Hans Puxbaum, Alexandre Caseiro, Casimiro Pio, and Michel Legrand. 2007. "Source apportionment of PM2. 5 organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and fossil/biogenic origin." *Journal of Geophysical Research: Atmospheres* no. 112 (D23).

Grimmer, Gernot, Juergen Jacob, Klaus Werner Naujack, and Gerhard Dettbarn. 1983. "Determination of polycyclic aromatic compounds emitted from brown-coal-fired residential stoves by gas chromatography/mass spectrometry." *Analytical Chemistry* no. 55 (6):892-900.

Gu, Zeping, Jialiang Feng, Wenliang Han, Li Li, Minghong Wu, Jiamo Fu, and Guoying Sheng. 2010. "Diurnal variations of polycyclic aromatic hydrocarbons associated with PM2. 5 in Shanghai, China." *Journal of Environmental Sciences* no. 22 (3):389-396.

Guo, H, SC Lee, KF Ho, XM Wang, and SC Zou. 2003. "Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong." *Atmospheric Environment* no. 37 (38):5307-5317.

Hallquist, Mattias, JC Wenger, Urs Baltensperger, Y Rudich, David Simpson, M Claeys, J Dommen, NM Donahue, C George, and AH Goldstein. 2009. "The formation, properties and impact of secondary organic aerosol: current and emerging issues." *Atmospheric Chemistry and Physics* no. 9 (14):5155-5236.

Han, JS, KJ Moon, SJ Lee, YJ Kim, SY Ryu, SS Cliff, and SM Yi. 2005. "Size-resolved source apportionment of ambient particles by positive matrix factorization." *Atmospheric Chemistry and Physics Discussions* no. 5 (4):5223-5252.

Han, JS, KJ Moon, SJ Lee, YJ Kim, SY Ryu, SS Cliff, and SM Yi. 2006. "Size-resolved source apportionment of ambient particles by positive matrix factorization at Gosan background site in East Asia." *Atmospheric Chemistry and Physics* no. 6 (1):211-223.

Harrison, Roy M, DJT Smith, and L Luhana. 1996. "Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK." *Environmental Science & Technology* no. 30 (3):825-832.

Henry, Ronald C, and Gary A Norris. 2002. "EPA Unmix 2.3 User Guide." *US Environmental Protection Agency: Washington, DC*.

Heo, J-B, PK Hopke, and S-M Yi. 2009. "Source apportionment of PM 2.5 in Seoul, Korea." *Atmospheric Chemistry and Physics* no. 9 (14):4957-4971.

Ho, KF, JJ Cao, SC Lee, Kimitaka Kawamura, RJ Zhang, Judith C Chow, and John G Watson. 2007. "Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls

in the urban atmosphere of China." *Journal of Geophysical Research: Atmospheres* no. 112 (D22).

Hogg, James C, Fanny Chu, Soraya Utokaparch, Ryan Woods, W Mark Elliott, Liliana Buzatu, Ruben M Cherniack, Robert M Rogers, Frank C Sciurba, and Harvey O Coxson. 2004. "The nature of small-airway obstruction in chronic obstructive pulmonary disease." *New England Journal of Medicine* no. 350 (26):2645-2653.

Hopke, Philip K. 2003. "Recent developments in receptor modeling." *Journal of chemometrics* no. 17 (5):255-265.

Hu, DM, L Peng, HL Bai, L Mu, F Han, XF Liu, HD Ji, and PJ Zhang. 2013. "Distribution and source apportionment of n-alkanes in atmospheric particle in Taiyuan, China." *Huan jing ke xue= Huanjing kexue/[bian ji, Zhongguo ke xue yuan huan jing ke xue wei yuan hui" Huan jing ke xue" bian ji wei yuan hui.]* no. 34 (10):3733-3740.

Huang, Xiao-Feng, Ling-Yan He, Min Hu, and Yuan-Hang Zhang. 2006. "Annual variation of particulate organic compounds in PM 2.5 in the urban atmosphere of Beijing." *Atmospheric Environment* no. 40 (14):2449-2458.

Huang, Xiao-Feng, Min Hu, Ling-Yan He, and Xiao-Yan Tang. 2005. "Chemical characterization of water-soluble organic acids in PM 2.5 in Beijing, China." *Atmospheric environment* no. 39 (16):2819-2827.

Hyo, Yun Jin Joseph, and Avvari V Mohan. "A Comparative Study of the Dynamics of Innovation Systems in three Clusters from Korea and Malaysia."

Jeong, Ju-Hee, Zang-Ho Shon, Minsung Kang, Sang-Keun Song, Yoo-Keun Kim, Jinsoo Park, and Hyunjae Kim. 2017. "Comparison of source apportionment of PM 2.5 using receptor models in the main hub port city of East Asia: Busan." *Atmospheric Environment* no. 148:115-127.

Jeong, Ukkyo, Jhoon Kim, Hanlim Lee, Jinsang Jung, Young J Kim, Chul H Song, and Ja-Ho Koo. 2011. "Estimation of the contributions of long range transported aerosol in East Asia to carbonaceous aerosol and PM concentrations in Seoul, Korea using highly time resolved measurements: a PSCF model approach." *Journal of Environmental Monitoring* no. 13 (7):1905-1918.

Jeong, YeongJin, and InJo Hwang. 2015. "Source Apportionment of PM 2.5 in Gyeongsan Using the PMF Model." *Journal of Korean Society for Atmospheric Environment* no. 31 (6):508-519.

Jun Li, Jian, Ge Hui Wang, Xin Ming Wang, Jun Ji Cao, Tao Sun, Chun Lei Cheng, Jing Jing Meng, TA Feng Hu, and sui Xin Liu. 2013. "Abundance, composition and source of atmospheric PM2. 5 at a remote site in the Tibetan Plateau, China." *Tellus B: Chemical and Physical Meteorology* no. 65

(1):20281.

Kang, Byung-Wook, Hak-Sung Lee, Jong-Ho Kim, Ji-Hyung Hong, Rok-Ho Kim, Young-Kyo Seo, Jin-Seok Han, Kyung-Min Baek, Min-Ji Kim, and Sung-Ok Baek. 2016. "Distribution of Airborne Hexavalent chromium concentrations in Large Industrial complexes in Korea." *Asian Journal of Atmospheric Environment* no. 10 (4):208-216.

Kang, Choong-Min, Byung-Wook Kang, and Hak Sung Lee. 2006. "Source identification and trends in concentrations of gaseous and fine particulate principal species in Seoul, South Korea." *Journal of the Air & Waste Management Association* no. 56 (7):911-921.

Kawamura, Kimitaka, and Kouichi Ikushima. 1993. "Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere." *Environmental Science & Technology* no. 27 (10):2227-2235.

Kawamura, Kimitaka, and Isaac R Kaplan. 1987. "Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air." *Environmental Science & Technology* no. 21 (1):105-110.

Kim, K-H, VK Mishra, C-H Kang, K-C Choi, YJ Kim, DS Kim, Y-H Youn, and J-H Lee. 2006. "The metallic composition of aerosols at three monitoring sites in Korea during winter 2002." *Environmental monitoring and assessment* no. 121 (1):379-397.

Kim, Ki-Hyun, Ehsanul Kabir, and Shamin Kabir. 2015. "A review on the human health impact of airborne particulate matter." *Environment international* no. 74:136-143.

Kim, Ki-Hyun, Dong-Sool Kim, and Tae-Jung Lee. 1997. "The temporal variabilities in the concentrations of airborne lead and its relationship to aerosol behavior." *Atmospheric Environment* no. 31 (20):3449-3458.

Kim, Ki-Hyun, and Min-Young Kim. 2003. "The effects of Asian Dust on particulate matter fractionation in Seoul, Korea during spring 2001." *Chemosphere* no. 51 (8):707-721.

Kim, Mo-Keun, and Wan-Kuen Jo. 2006. "Elemental composition and source characterization of airborne PM10 at residences with relative proximities to metal-industrial complex." *International archives of occupational and environmental health* no. 80 (1):40-50.

Kim, Yoo Jung, Jung-Hun Woo, Young-Il Ma, Suhyang Kim, Jung Sik Nam, Hakyoung Sung, Ki-Chul Choi, Jihyun Seo, Jeong Su Kim, and Chang-Hee Kang. 2009. "Chemical characteristics of long-range transport aerosol at background sites in Korea." *Atmospheric Environment* no. 43 (34):5556-5566.

Koch, Matthias. 2000. "Airborne fine particulates in the environment: a review of

health effect studies, monitoring data and emission inventories."

Koton, Silvia, Noa Molshatzki, Vicki Myers, David M Broday, Yaacov Drory, David M Steinberg, and Yariv Gerber. 2013. "Cumulative exposure to particulate matter air pollution and long-term post-myocardial infarction outcomes." *Preventive medicine* no. 57 (4):339-344.

Lee, Patrick KH, Jeffrey R Brook, Ewa Dabek-Zlotorzynska, and Scott A Mabury. 2003. "Identification of the major sources contributing to PM2. 5 observed in Toronto." *Environmental science & technology* no. 37 (21):4831-4840.

Lee, Taehyoung, Jinsoo Choi, Gangwoong Lee, Junyoung Ahn, Jin Soo Park, Samuel A Atwood, Misha Schurman, Yongjoo Choi, Yoomi Chung, and Jeffrey L Collett. 2015. "Characterization of aerosol composition, concentrations, and sources at Baengnyeong Island, Korea using an aerosol mass spectrometer." *Atmospheric Environment* no. 120:297-306.

Li, Min, Stephen R McDow, David J Tollerud, and Monica A Mazurek. 2006. "Seasonal abundance of organic molecular markers in urban particulate matter from Philadelphia, PA." *Atmospheric Environment* no. 40 (13):2260-2273.

Lim, Jong-Myoung, Jin-Hong Lee, Jong-Hwa Moon, Yong-Sam Chung, and Ki-Hyun Kim. 2010a. "Airborne PM10 and metals from multifarious sources in an industrial complex area." *Atmospheric Research* no. 96 (1):53-64.

Lim, Jong-Myoung, Jin-Hong Lee, Jong-Hwa Moon, Yong-Sam Chung, and Ki-Hyun Kim. 2010b. "Source apportionment of PM10 at a small industrial area using Positive Matrix Factorization." *Atmospheric Research* no. 95 (1):88-100.

Lin, Lin, Milton L Lee, and Delbert J Eatough. 2010. "Review of recent advances in detection of organic markers in fine particulate matter and their use for source apportionment." *Journal of the Air & Waste Management Association* no. 60 (1):3-25.

Lin, Peng, Min Hu, Z Deng, J Slanina, S Han, Y Kondo, N Takegawa, Y Miyazaki, Y Zhao, and N Sugimoto. 2009. "Seasonal and diurnal variations of organic carbon in PM2. 5 in Beijing and the estimation of secondary organic carbon." *Journal of Geophysical Research: Atmospheres* no. 114 (D2).

Liu, Shuzhen, Shu Tao, Wenxin Liu, Yanan Liu, Han Dou, Jingyu Zhao, Luguang Wang, Jingfei Wang, Zaifeng Tian, and Yuan Gao. 2007. "Atmospheric polycyclic aromatic hydrocarbons in north China: a winter-time study." *Environmental science & technology* no. 41 (24):8256-8261.

Liu, Tengyu, Xinming Wang, Qihou Hu, Wei Deng, Yanli Zhang, Xiang Ding, X Fu, F Bernard, Zengxiang Zhang, and Shikun Lü. 2016. "Formation of secondary aerosols from gasoline vehicle exhaust when mixing with SO 2."

Atmospheric Chemistry and Physics no. 16 (2):675-689.

Liu, Yan-Ju, Ting-Ting Zhang, Qing-Yang Liu, Ren-Jian Zhang, Zhen-Quan Sun, and Mei-Gen Zhang. 2014. "Seasonal variation of physical and chemical properties in TSP, PM10 and PM2. 5 at a roadside site in Beijing and their influence on atmospheric visibility." *Aerosol Air Qual. Res* no. 14 (3):954-969.

Liu, ZP. 2003. "Lead poisoning combined with cadmium in sheep and horses in the vicinity of non-ferrous metal smelters." *Science of the Total Environment* no. 309 (1):117-126.

Locker, Harry Byrne. 1988. The use of levoglucosan to assess the environmental impact of residential wood-burning on air quality. Dartmouth Coll., Hanover, NH (USA).

Louie, Peter KK, John G Watson, Judith C Chow, Antony Chen, Della WM Sin, and Alexis KH Lau. 2005. "Seasonal characteristics and regional transport of PM 2.5 in Hong Kong." *Atmospheric Environment* no. 39 (9):1695-1710.

Madrigano, Jaime, Itai Kloog, Robert Goldberg, Brent A Coull, Murray A Mittleman, and Joel Schwartz. 2013. "Long-term exposure to PM2. 5 and incidence of acute myocardial infarction." *Environmental Health Perspectives (Online)* no. 121 (2):192.

Manoli, E, A Kouras, and C Samara. 2004. "Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece." *Chemosphere* no. 56 (9):867-878.

Manoli, E, D Voutsa, and C Samara. 2002. "Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece." *Atmospheric Environment* no. 36 (6):949-961.

Mazquiarán, Miguel A Barrero, and Lourdes Cantón Ortiz de Pinedo. 2007. "Organic composition of atmospheric urban aerosol: Variations and sources of aliphatic and polycyclic aromatic hydrocarbons." *Atmospheric Research* no. 85 (3):288-299.

Miyazaki, Y, Y Kondo, N Takegawa, Y Komazaki, M Fukuda, K Kawamura, M Mochida, K Okuzawa, and RJ Weber. 2006. "Time-resolved measurements of water-soluble organic carbon in Tokyo." *Journal of Geophysical Research: Atmospheres* no. 111 (D23).

Molnár, A, E Mészáros, HC Hansson, H Karlsson, A Gelencsér, GY Kiss, and Z Krivácsy. 1999. "The inportance of organic and elemental carbon in the fine atmospheric aerosol particles." *Atmospheric Environment* no. 33 (17):2745-2750.

Moon, KJ, JS Han, YS Ghim, and YJ Kim. 2008. "Source apportionment of fine carbonaceous particles by positive matrix factorization at Gosan background

site in East Asia." *Environment international* no. 34 (5):654-664.

Moon, KJ, JS Han, BJ Kong, IR Jung, Steven S Cliff, Thomas A Cahill, and Kelvin D Perry. 2006. "Size-resolved source apportionment of ambient particles by positive matrix factorization at Gosan, Jeju Island during ACE-Asia." *Journal of Korean Society for Atmospheric Environment* no. 22 (5):590-603.

Mulawa, Patricia A, Steven H Cadle, Kenneth Knapp, Roy Zweidinger, Richard Snow, Randy Lucas, and Joseph Goldbach. 1997. "Effect of ambient temperature and E-10 fuel on primary exhaust particulate matter emissions from light-duty vehicles." *Environmental science & technology* no. 31 (5):1302-1307.

Norris, GA, R Duvall, SG Brown, and S Bai. 2014. EPA Positive Matrix Factorization (PMF) 5.0 fundamentals and User Guide Prepared for the US Environmental Protection Agency Office of Research and Development, Washington. DC EPA/600/R-14/108.

Norris, Gary, Ram Vedantham, Katie Wade, Steve Brown, Jeff Prouty, and Chuck Foley. 2008. "EPA positive matrix factorization (PMF) 3.0 fundamentals & user guide." *Prepared for the US Environmental Protection Agency, Washington, DC, by the National Exposure Research Laboratory, Research Triangle Park*.

Oh, Hye-Ryun, Chang-Hoi Ho, Jinwon Kim, Deliang Chen, Seungmin Lee, Yong-Sang Choi, Lim-Seok Chang, and Chang-Keun Song. 2015. "Long-range transport of air pollutants originating in China: a possible major cause of multi-day high-PM 10 episodes during cold season in Seoul, Korea." *Atmospheric Environment* no. 109:23-30.

Oh, Mi-Seok, Tae-Jung Lee, and Dong-Sool Kim. 2009. "Source identification of ambient size-by-size particulate using the positive matrix factorization model on the border of Yongin and Suwon." *Journal of Korean Society for Atmospheric Environment* no. 25 (2):108-121.

Oh, Mi-Seok, Tae-Jung Lee, and Dong-Sool Kim. 2011. "Quantitative source apportionment of size-segregated particulate matter at urbanized local site in Korea." *Aerosol and Air Quality Resarch* no. 11 (3):247-264.

Ohura, Takeshi, Takashi Amagai, Masahiro Fusaya, and Hidetsuru Matsushita. 2004. "Polycyclic aromatic hydrocarbons in indoor and outdoor environments and factors affecting their concentrations." *Environmental science & technology* no. 38 (1):77-83.

Organization, World Health. 2000. "Air quality guidelines for Europe."

Organization, World Health. 2015. "Economic cost of the health impact of air pollution in Europe: Clean air, health and wealth." *WHO Regional office for Europe, Copenhagen*.

Paatero, Pentti. 1997. "Least squares formulation of robust non-negative factor analysis." *Chemometrics and intelligent laboratory systems* no. 37 (1):23-35.

Paatero, Pentti, and Unto Tapper. 1994. "Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values." *Environmetrics* no. 5 (2):111-126.

Pace, TG, and JG Watson. 1987. Protocol for applying and validating the CMB (chemical mass balance) model. Environmental Protection Agency, Research Triangle Park, NC (USA). Monitoring and Data Analysis Div.

Pacini, E, M Guarnieri, and M Nepi. 2006. "Pollen carbohydrates and water content during development, presentation, and dispersal: a short review." *Protoplasma* no. 228 (1):73-77.

Park, Seung S, Young J Kim, and Kochy Fung. 2001. "Characteristics of PM 2.5 carbonaceous aerosol in the Sihwa industrial area, Korea." *Atmospheric Environment* no. 35 (4):657-665.

Park, Seung Shik, Min-Suk Bae, James J Schauer, Young J Kim, Sung Yong Cho, and Seung Jai Kim. 2006. "Molecular composition of PM 2.5 organic aerosol measured at an urban site of Korea during the ACE-Asia campaign." *Atmospheric Environment* no. 40 (22):4182-4198.

Pekney, Natalie J, Cliff I Davidson, Liming Zhou, and Philip K Hopke. 2006. "Application of PSCF and CPF to PMF-modeled sources of PM2. 5 in Pittsburgh." *Aerosol Science and Technology* no. 40 (10):952-961.

Pio, CA, CA Alves, and AC Duarte. 2001. "Identification, abundance and origin of atmospheric organic particulate matter in a Portuguese rural area." *Atmospheric Environment* no. 35 (8):1365-1375.

Raaschou-Nielsen, Ole, Zorana J Andersen, Rob Beelen, Evangelia Samoli, Massimo Stafoggia, Gudrun Weinmayr, Barbara Hoffmann, Paul Fischer, Mark J Nieuwenhuijsen, and Bert Brunekreef. 2013. "Air pollution and lung cancer incidence in 17 European cohorts: prospective analyses from the European Study of Cohorts for Air Pollution Effects (ESCAPE)." *The lancet oncology* no. 14 (9):813-822.

Ram, Kirpa, MM Sarin, and SN Tripathi. 2012. "Temporal trends in atmospheric PM2. 5, PM10, elemental carbon, organic carbon, water-soluble organic carbon, and optical properties: impact of biomass burning emissions in the Indo-Gangetic Plain." *Environmental science & technology* no. 46 (2):686-695.

Ray, Joshua, and Stephen R McDow. 2005. "Dicarboxylic acid concentration trends and sampling artifacts." *Atmospheric Environment* no. 39 (40):7906-7919.

Rogge, Wolfgang F, Lynn M Hildemann, Monica A Mazurek, Glen R Cass, and

Bernd RT Simoneit. 1993. "Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks." *Environmental Science & Technology* no. 27 (9):1892-1904.

Rogge, Wolfgang F, Monica A Mazurek, Lynn M Hildemann, Glen R Cass, and Bernd RT Simoneit. 1993. "Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation." *Atmospheric Environment. Part A. General Topics* no. 27 (8):1309-1330.

Rogge, Wolfgang F, Monica A Mazurek, Lynn M Hildemann, Bernd RT Simoneit, and Glen R Cass. 1991. "Determination of organic compounds present in airborne particulate matter."

Samara, C, Th Kouimtzis, R Tsitouridou, G Kanias, and V Simeonov. 2003. "Chemical mass balance source apportionment of PM 10 in an industrialized urban area of Northern Greece." *Atmospheric environment* no. 37 (1):41-54.

Saylor, Rick D, Eric S Edgerton, and Benjamin E Hartsell. 2006. "Linear regression techniques for use in the EC tracer method of secondary organic aerosol estimation." *Atmospheric Environment* no. 40 (39):7546-7556.

Schauer, James J, BT Mader, JT Deminter, G Heidemann, MS Bae, John H Seinfeld, RC Flagan, RA Cary, D Smith, and BJ Huebert. 2003. "ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon." *Environmental science & technology* no. 37 (5):993-1001.

Schauer, James J, Wolfgang F Rogge, Lynn M Hildemann, Monica A Mazurek, Glen R Cass, and Bernd RT Simoneit. 1996. "Source apportionment of airborne particulate matter using organic compounds as tracers." *Atmospheric Environment* no. 30 (22):3837-3855.

Schlesinger, Richard B. 2007. "The health impact of common inorganic components of fine particulate matter (PM2. 5) in ambient air: a critical review." *Inhalation toxicology* no. 19 (10):811-832.

Sciare, Jean, Odile d'Argouges, Roland Sarda-Estève, Cécile Gaimoz, Cristina Dolgorouky, Nicolas Bonnaire, Olivier Favez, Bernard Bonsang, and Valérie Gros. 2011. "Large contribution of water-insoluble secondary organic aerosols in the region of Paris (France) during wintertime." *Journal of Geophysical Research: Atmospheres* no. 116 (D22).

Shi, Ji Ping, and Roy M Harrison. 1999. "Investigation of ultrafine particle formation during diesel exhaust dilution." *Environmental Science & Technology* no. 33 (21):3730-3736.

Simoneit, Bernd RT. 1986. "Characterization of organic constituents in aerosols in relation to their rigin and transport: a review." *International Journal of Environmental Analytical Chemistry* no. 23 (3):207-237.

Simoneit, Bernd RT. 1989. "Organic matter of the troposphere—V: application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations." *Journal of Atmospheric Chemistry* no. 8 (3):251-275.

Simoneit, Bernd RT, Vladimir O Elias, Minoru Kobayashi, Kimitaka Kawamura, Ahmed I Rushdi, Patricia M Medeiros, Wolfgang F Rogge, and Borys M Didyk. 2004. "Sugars dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter." *Environmental Science & Technology* no. 38 (22):5939-5949.

Simoneit, Bernd RT, and Monica A Mazurek. 1982. "Organic matter of the troposphere—II.⁎⁎ For Part I, see Simoneit et al.(1977). Natural background of biogenic lipid matter in aerosols over the rural western united states." *Atmospheric Environment (1967)* no. 16 (9):2139-2159.

Simoneit, Bernd RT, James J Schauer, CG Nolte, Daniel R Oros, Vladimir O Elias, MP Fraser, WF Rogge, and Glen R Cass. 1999. "Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles." *Atmospheric Environment* no. 33 (2):173-182.

Snyder, David C, Andrew P Rutter, Ryan Collins, Chris Worley, and James J Schauer. 2009. "Insights into the origin of water soluble organic carbon in atmospheric fine particulate matter." *Aerosol Science and Technology* no. 43 (11):1099-1107.

Stafoggia, Massimo, Alexandra Schneider, Josef Cyrys, Evangelia Samoli, Zorana Jovanovic Andersen, Getahun Bero Bedada, Tom Bellander, Giorgio Cattani, Konstantinos Eleftheriadis, and Annunziata Faustini. 2017. "Association between short-term exposure to ultrafine particles and mortality in eight European urban areas." *Epidemiology*.

Straif, K, A Cohen, J Samet, and International Agency for Research on Cancer. 2013. "IARC Scientific Publication No. 161: Air Pollution and Cancer." *World Health Organization, Geneva*.

Sullivan, Ryan C, and Kimberly A Prather. 2007. "Investigations of the diurnal cycle and mixing state of oxalic acid in individual particles in Asian aerosol outflow." *Environmental Science Technology* no. 41 (23):8062-8069.

Sun, Yele, Guoshun Zhuang, Ying Wang, Lihui Han, Jinghua Guo, Mo Dan, Wenjie Zhang, Zifa Wang, and Zhengping Hao. 2004. "The air-borne particulate pollution in Beijing—concentration, composition, distribution and sources." *Atmospheric Environment* no. 38 (35):5991-6004.

Swietlicki, Erik, Sanjiv Puri, Hans-Christen Hansson, and Hans Edner. 1996. "Urban air pollution source apportionment using a combination of aerosol and gas monitoring techniques." *Atmospheric Environment* no. 30 (15):2795-2809.

Tan, Jihua, Songjun Guo, Yongliang Ma, Jingchun Duan, Yuan Cheng, Kebin He, and Fumo Yang. 2011. "Characteristics of particulate PAHs during a typical haze episode in Guangzhou, China." *Atmospheric Research* no. 102 (1):91-98.

Taylor, David A. 2002. "Dust in the wind." *Environmental Health Perspectives* no. 110 (2):A80.

Thurston, George D, and John D Spengler. 1985. "A multivariate assessment of meteorological influences on inhalable particle source impacts." *Journal of Climate and applied meteorology* no. 24 (11):1245-1256.

Tobiszewski, Marek, and Jacek Namieśnik. 2012. "PAH diagnostic ratios for the identification of pollution emission sources." *Environmental Pollution* no. 162:110-119.

Tsapakis, Manolis, Evaggelia Lagoudaki, Euripides G Stephanou, Ilias G Kavouras, Petros Koutrakis, Pedro Oyola, and Dietrich von Baer. 2002. "The composition and sources of PM 2.5 organic aerosol in two urban areas of Chile." *Atmospheric Environment* no. 36 (23):3851-3863.

Turn, SQ, BM Jenkins, JC Chow, LC Pritchett, D Campbell, T Cahill, and SA Whalen. 1997. "Elemental characterization of particulate matter emitted from biomass burning: Wind tunnel derived source profiles for herbaceous and wood fuels." *Journal of Geophysical Research: Atmospheres* no. 102 (D3):3683-3699.

Turpin, Barbara J, and James J Huntzicker. 1995. "Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS." *Atmospheric Environment* no. 29 (23):3527-3544.

Uberol, Mohit, and Farhang Shadman. 1991. "High-temperature removal of cadmium compounds using solid sorbents." *Environmental Science and Technology* no. 25 (7):1285-1289.

Venkataraman, Chandra, James M Lyons, and Sheldon K Friedlander. 1994. "Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization." *Environmental science & technology* no. 28 (4):555-562.

Viana, M, TAJ Kuhlbusch, X Querol, A Alastuey, RM Harrison, PK Hopke, W Winiwarter, M Vallius, Sönke Szidat, and ASH Prévôt. 2008. "Source apportionment of particulate matter in Europe: a review of methods and results." *Journal of aerosol science* no. 39 (10):827-849.

Wang, Gehui, Kimitaka Kawamura, and Meehye Lee. 2009. "Comparison of organic compositions in dust storm and normal aerosol samples collected at Gosan, Jeju Island, during spring 2005." *Atmospheric Environment* no. 43 (2):219-

227.

Wang, Gehui, Kimitaka Kawamura, Xin Zhao, Qiuge Li, Zhaoxia Dai, and Hongyun Niu. 2007. "Identification, abundance and seasonal variation of anthropogenic organic aerosols from a mega-city in China." *Atmospheric Environment* no. 41 (2):407-416.

Wang, SX, Bin Zhao, SY Cai, Z Klimont, CP Nielsen, T Morikawa, JH Woo, Y Kim, X Fu, and JY Xu. 2014. "Emission trends and mitigation options for air pollutants in East Asia." *Atmospheric Chemistry and Physics* no. 14 (13):6571-6603.

Wang, Xiaobin, O Oenema, WB Hoogmoed, UD Perdok, and Dianxiong Cai. 2006. "Dust storm erosion and its impact on soil carbon and nitrogen losses in northern China." *Catena* no. 66 (3):221-227.

Wang, Yan, Liuhua Shi, Mihye Lee, Pengfei Liu, Qian Di, Antonella Zanobetti, and Joel D Schwartz. 2017. "Long-term exposure to PM2. 5 and mortality among older adults in the Southeastern US." *Epidemiology*.

Wang, Yungang, Philip K Hopke, Xiaoyan Xia, Oliver V Rattigan, David C Chalupa, and Mark J Utell. 2012. "Source apportionment of airborne particulate matter using inorganic and organic species as tracers." *Atmospheric Environment* no. 55:525-532.

Xie, Yang, Hancheng Dai, Huijuan Dong, Tatsuya Hanaoka, and Toshihiko Masui. 2016. "Economic impacts from PM2. 5 pollution-related health effects in China: A provincial-Level analysis." *Environmental science & technology* no. 50 (9):4836-4843.

Yi, Seung-Muk, and InJo Hwang. 2014. "Source Identification and Estimation of Source Apportionment for Ambient PM 10 in Seoul, Korea." *Asian J. Atmos. Environ* no. 8 (3):115-125.

Yu, LI, Yan-bin WANG, GOU Xin, Yi-bing SU, and WANG Gang. 2006. "Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China." *Journal of Environmental Sciences* no. 18 (6):1124-1134.

Yue, Zhiwei, and Matthew P Fraser. 2004. "Polar organic compounds measured in fine particulate matter during TexAQS 2000." *Atmospheric Environment* no. 38 (20):3253-3261.

Zhang, Qiang, David G Streets, Kebin He, and Zbigniew Klimont. 2007. "Major components of China? s anthropogenic primary particulate emissions." *Environmental Research Letters* no. 2 (4):045027.

Zhang, Ting, Magda Claeys, Hélène Cachier, Shuping Dong, Wan Wang, Willy Maenhaut, and Xiande Liu. 2008. "Identification and estimation of the biomass burning contribution to Beijing aerosol using levoglucosan as a

molecular marker." *Atmospheric Environment* no. 42 (29):7013-7021.

Zhao, HY, Q Zhang, DB Guan, SJ Davis, Z Liu, H Huo, JT Lin, WD Liu, and KB He. 2015. "Assessment of China's virtual air pollution transport embodied in trade by using a consumption-based emission inventory." *Atmospheric Chemistry and Physics* no. 15 (10):5443-5456.

Supplementary Materials

Table S3-1. Operating conditions of GC/MSD (7890A/5975C, Agilent Technologies) used with organic compounds in this study

GC/MSD (7890A/5975C)		Operating conditions
Column	Part Number	DV-5MS (30 m × 0.25 mm × 0.25 μm), Agilent Technologies
	Stationary Phase	95% Dimethylsiloxane copolymer with 5% Diphenyl
Carrier	Carrier Gas	Helium
	Flow Rate	1 mL/min
Injector	Injection Volume	1 μL
	Injection Mode	Splitless mode
Temperature	Initial Temp.	60 °C for 1 min
	Rate of Temp.	6 °C/min to 310 °C
	Isothermal Pause	15 min at 310 °C
Detector	Solvent Delay	8 min
	Electron Energy	70eV

Table S3-2. Spike volume (μl) and Final spike concentration (ng/μl) of surrogate standard and internal standard used in this study

Organic group		Standard name	Spike Volume (μl)	Final spike conc. (ng/μl)
PAHs	Surrogate standard	Phenanthrene-d10	50	2.00
		Fluoranthene-d10	50	1.97
		Chrysene-d12	50	2.00
		Perylene-d12	50	2.00
		Benzo[ghi]perylene-d12	50	2.00
	*Internal standard	Pyrene-d10	2.5	523.5
n-Alkanes	Surrogate standard	Tetracosane-d50 (C24-d50)	50	2.01
		Triacontane-d62 (C30-d62)	50	1.98
		Hexatriacontane-d74 (C36-d74)	50	1.98
	Internal standard	Eicosane-d42	2.5	512.5
n-Alkanoic acids	Surrogate standard	Myristic-d27 acid	50	19.99
	Internal standard	Palmitic acid-d31	2.5	4998
Dicarboxylic acids	Surrogate standard	Succinic acid-d6	50	19.69
	Internal standard	Palmitic acid-d31	2.5	4998
Sugars	Surrogate standard	Levoglucosan-d7	50	20.06
	*Internal standard	Palmitic acid-d31	2.5	4998

Note: *Internal standard was added right before GC-MS analysis to monitor instrumental recovery efficiency

Table S3-3. PAHs recovery of SRM NIST 1649b Urban dust using the amount of 20 mg

PAHs compounds	Certified Value (mg/kg)	Measured Value (mg/kg)	Recovery (%)	RSD (%)
Phenanthrene	4.03 ± 0.06	2.64 ± 0.06	65.51 ±1.49	2.27
Anthracene	0.41 ± 0.00	0.79 ± 0.06	193.47 ± 15.72	8.12
Fluoranthene	6.24 ± 0.08	4.23 ± 0.18	67.73 ± 2.88	4.25
Pyrene	4.98 ± 0.14	3.57 ± 0.17	71.71 ± 3.51	4.90
Benz[a]anthracene	2.35 ± 0.12	1.54 ± 0.08	65.37 ± 3.43	5.24
Chrysene	3.05 ± 0.03	3.27 ± 0.07	107.27 ± 2.33	2.17
Benzo[b]fluoranthene	6.18 ± 0.18	4.57 ± 0.30	73.94 ± 4.88	6.59
Benzo[e]pyrene	2.97 ± 0.05	2.53 ± 0.06	85.03 ± 2.05	2.41
Benzo[a]pyrene	2.81 ± 0.38	1.26 ± 0.18	44.78 ± 6.38	14.26
Perylene	0.61 ± 0.01	0.47 ± 0.00	76.39 ± 0.74	0.97
Indeno[1,2,3-cd]pyrene	2.89 ± 0.16	2.27 ± 0.04	78.66 ± 1.39	1.77
Dibenz[a,h]anthracene	0.29 ± 0.00	0.46 ± 0.06	157.62 ± 19.88	12.61
Benzo[ghi]perylene	3.97 ± 0.04	2.98 ± 0.15	75.18 ± 3.69	4.91
Coronene	3.16 ± 0.05	1.49 ± 0.29	47.14 ± 9.02	19.14

Table S3-4. PCA results of Dicarboxylic acids compounds

	Identified sources	Factor 1	Factor 2	Factor 3	Communalities
Dicarboxylic acids (DCAs)	Malonic acid	.396	.085	**.861**	.905
	Methylmalonic acid	**.720**	.120	.582	.872
	Maleic acid	**.761**	.430	.203	.805
	Succinic acid	**.916**	-	.307	.933
	Methylsuccinic acid	**.946**	.119	.180	.941
	Methylmaleic acid	.573	**.713**	-	.837
	Fumaric acid	.396	.344	**.773**	.874
	Glutaric acid	**.902**	.065	.266	.889
	2-methylglutaric acid	**.868**	.313	.277	.928
	D-Malic acid	.578	.421	**.607**	.879
	Adipic acid	**.793**	.343	.347	.868
	Pimelic acid	.290	**.683**	.306	.644
	phthalic acid	**.737**	.438	.241	.793
	Suberic acid	.327	.547	.411	.575
	Iso-phthalic acid	.361	**.823**	.134	.826
	Tere-phthalic acid	.030	**.772**	.031	.598
	Azelaic acid	.051	**.967**	.045	.940
	Sebacic acid	.104	**.921**	.213	.904
	Undecanedionic acid	.167	**.910**	.250	.918
	Eigenvalues	11.514	3.359	1.058	
	Variance (%)	60.600	17.681	5.569	
	Cumulative (%)	60.600	78.281	83.849	

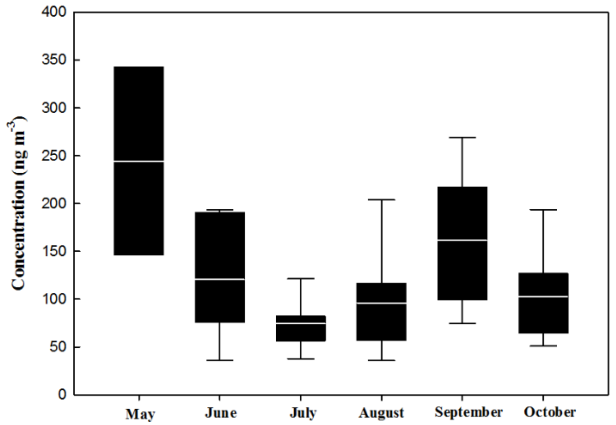

Fig. S3-1. Monthly Organic compounds mass concentration trends

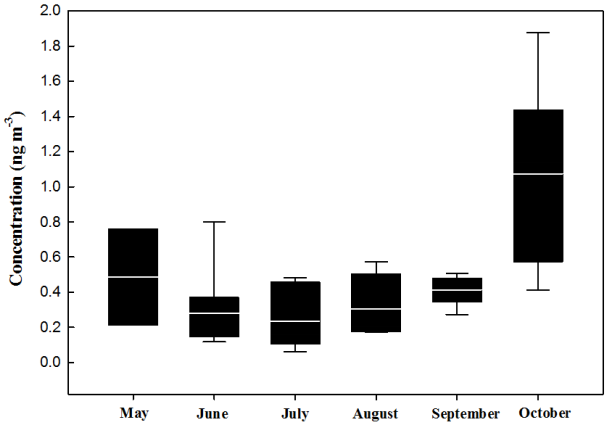

Fig. S3-2. Monthly PAHs mass concentration trends

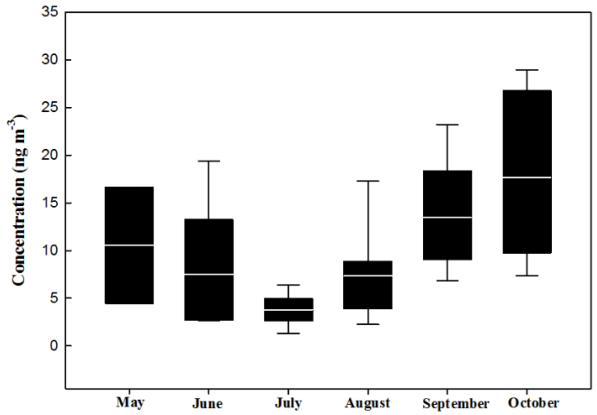

Fig. S3-3. Monthly n-Alkanes mass concentration trends

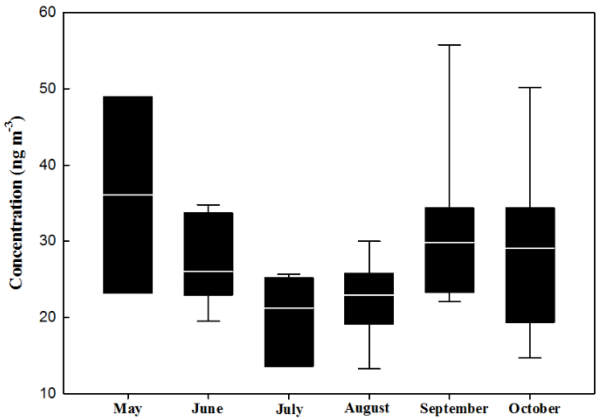

Fig. S3-4. Monthly n-Alkanoic acids mass concentration trends

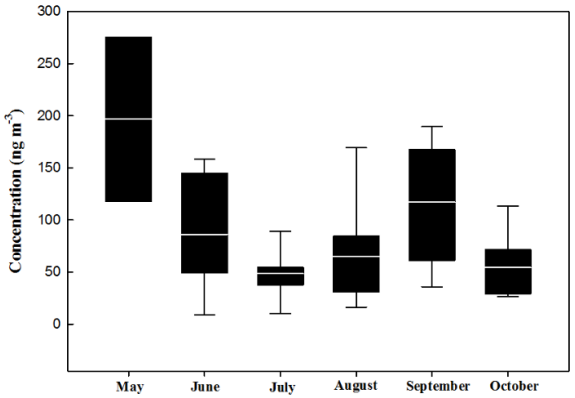

Fig. S3-5. Monthly DCAs mass concentration

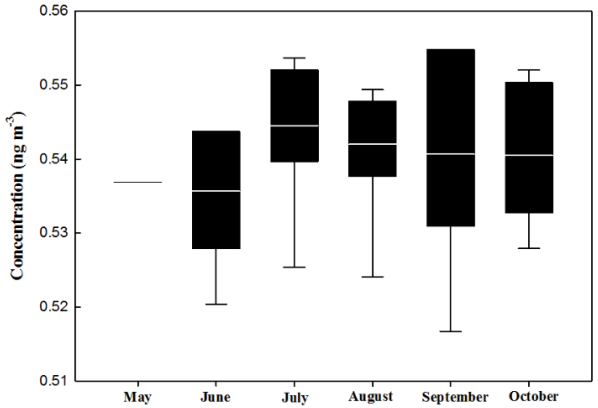

Fig. S3-6. Monthly Sugars mass concentration trends

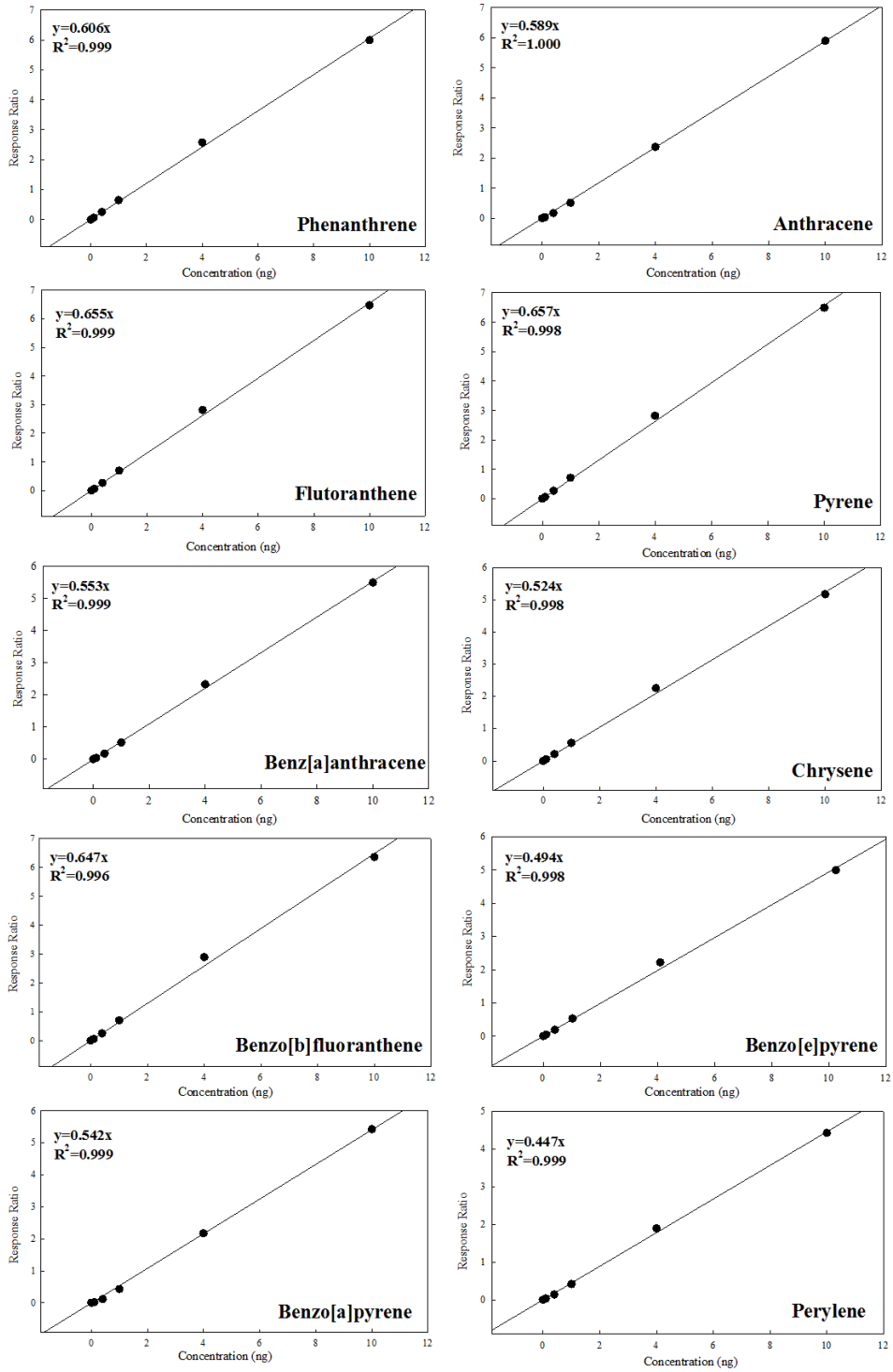

Fig. S3-7. Calibration curves of individual PAHs

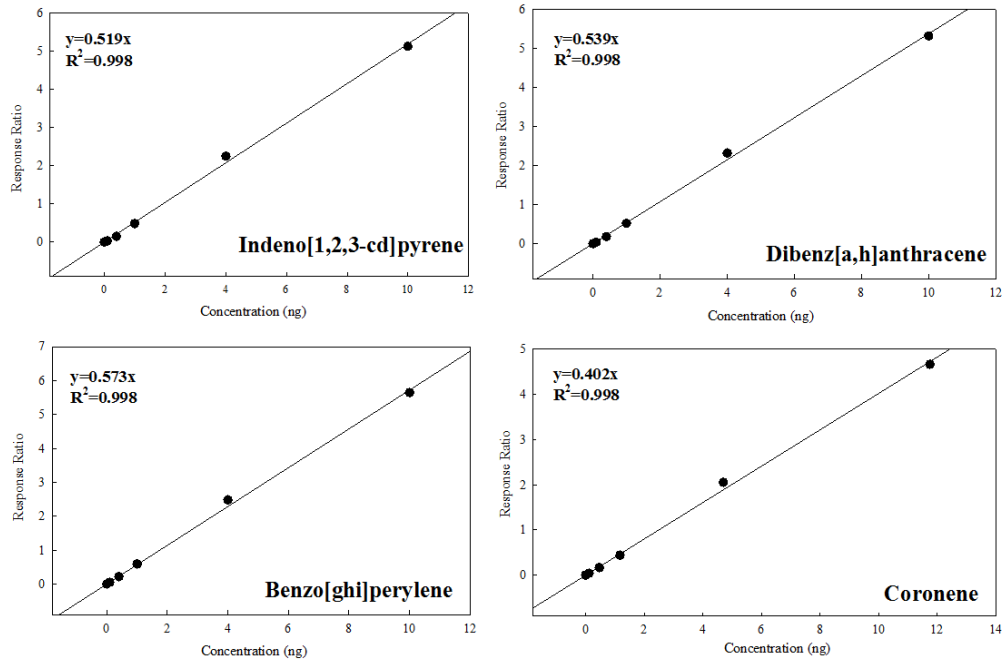

Fig. S3-7. (Continue)

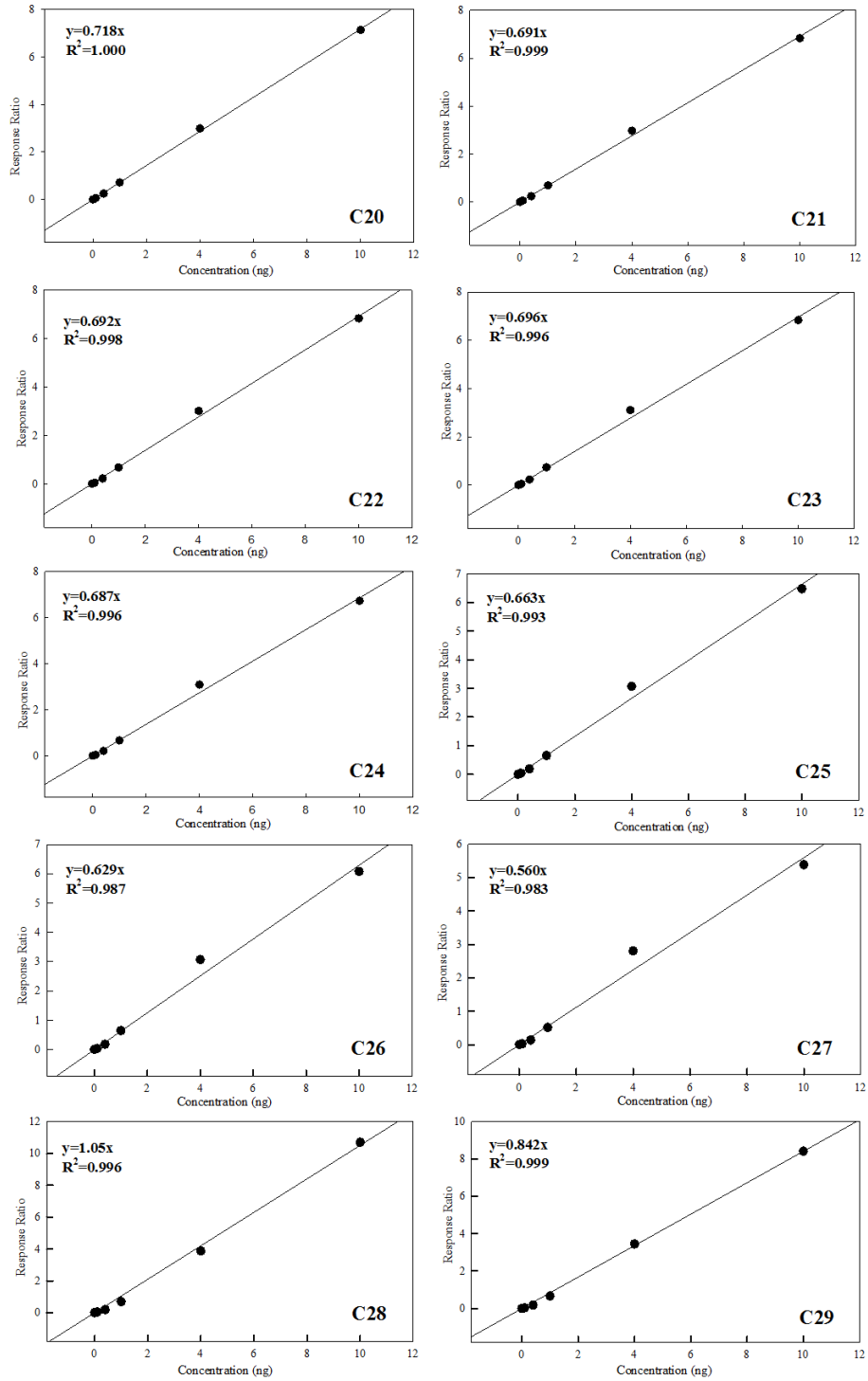

Fig. S3-8. Calibration curves of individual n-Alkanes

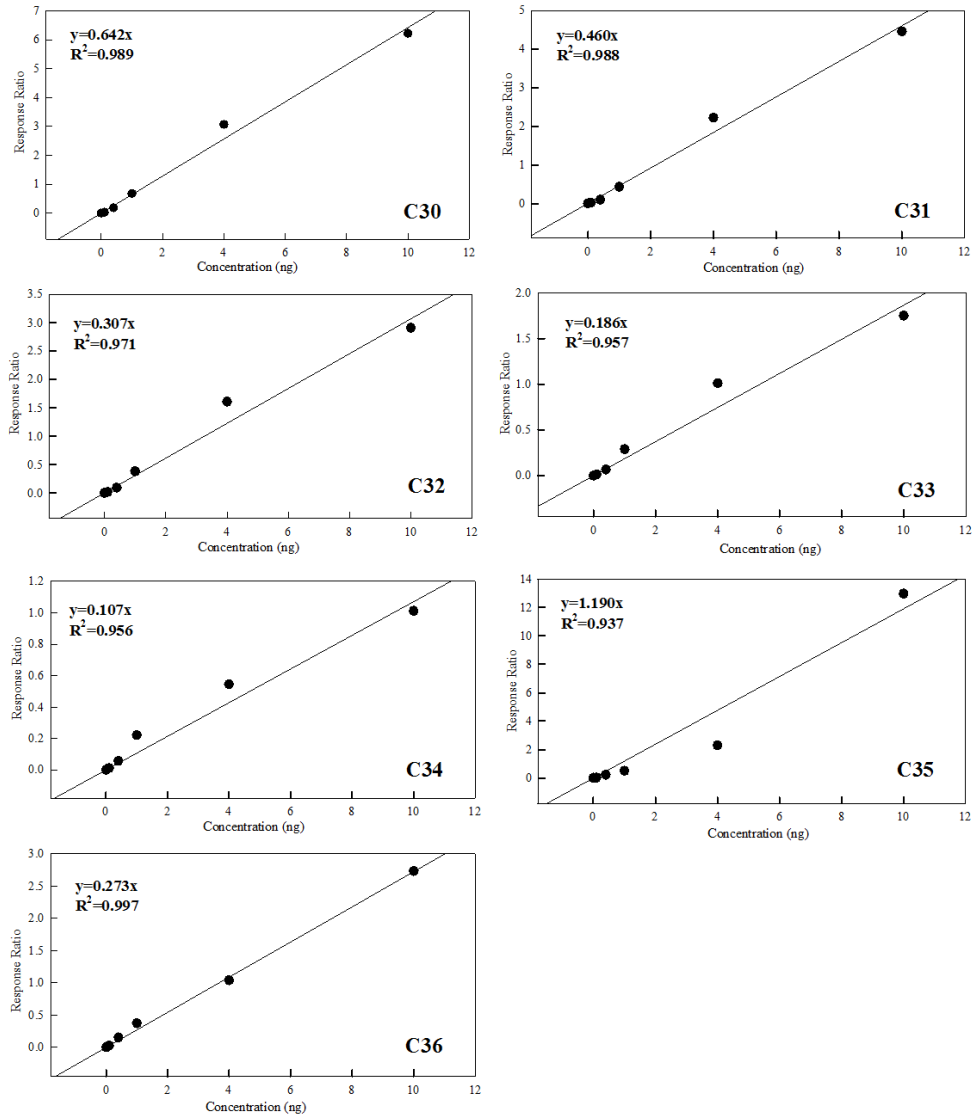

Fig. S3-8. (Continue)

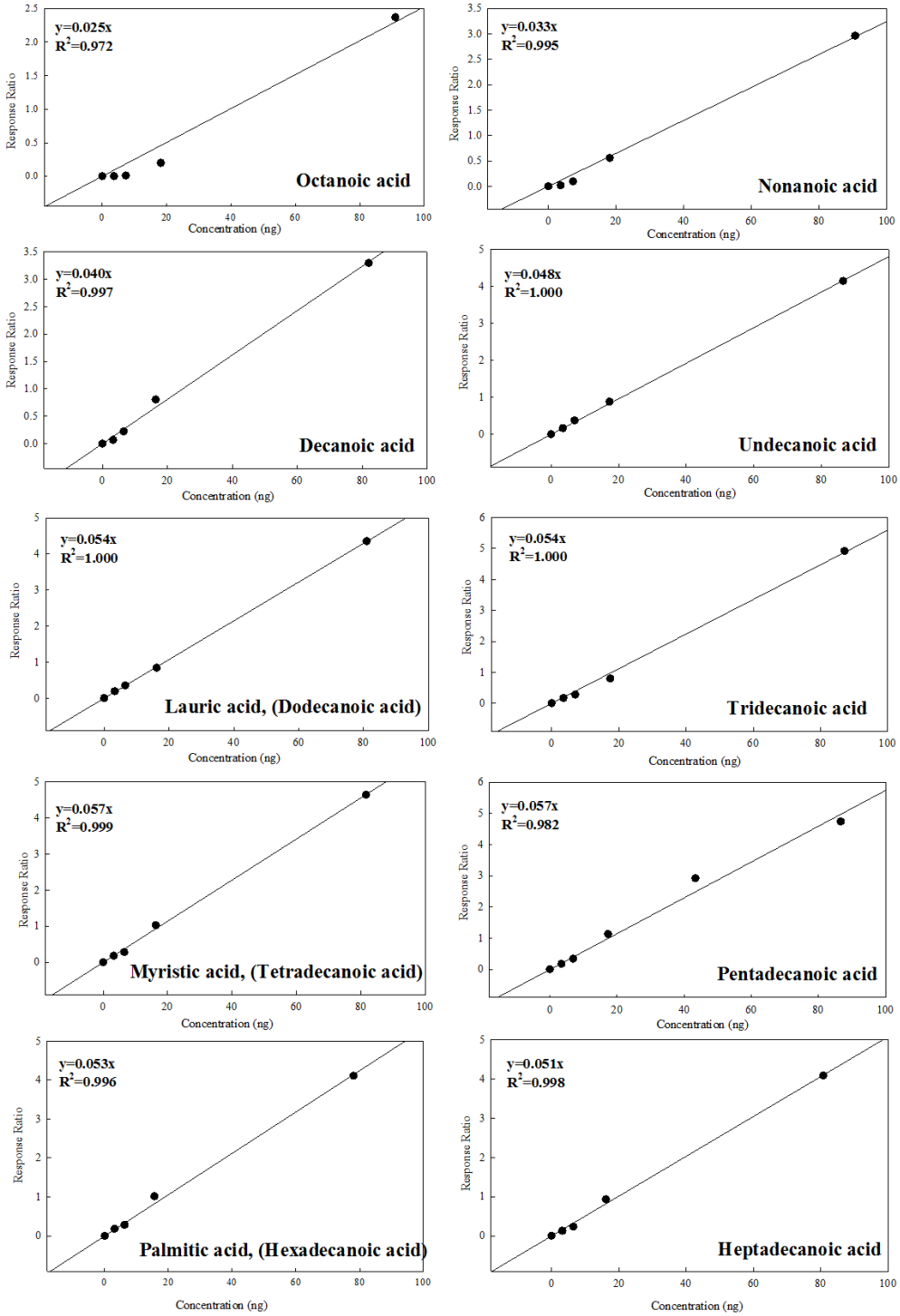

Fig. S3-9. Calibration curves of individual n-Alkanoic acids

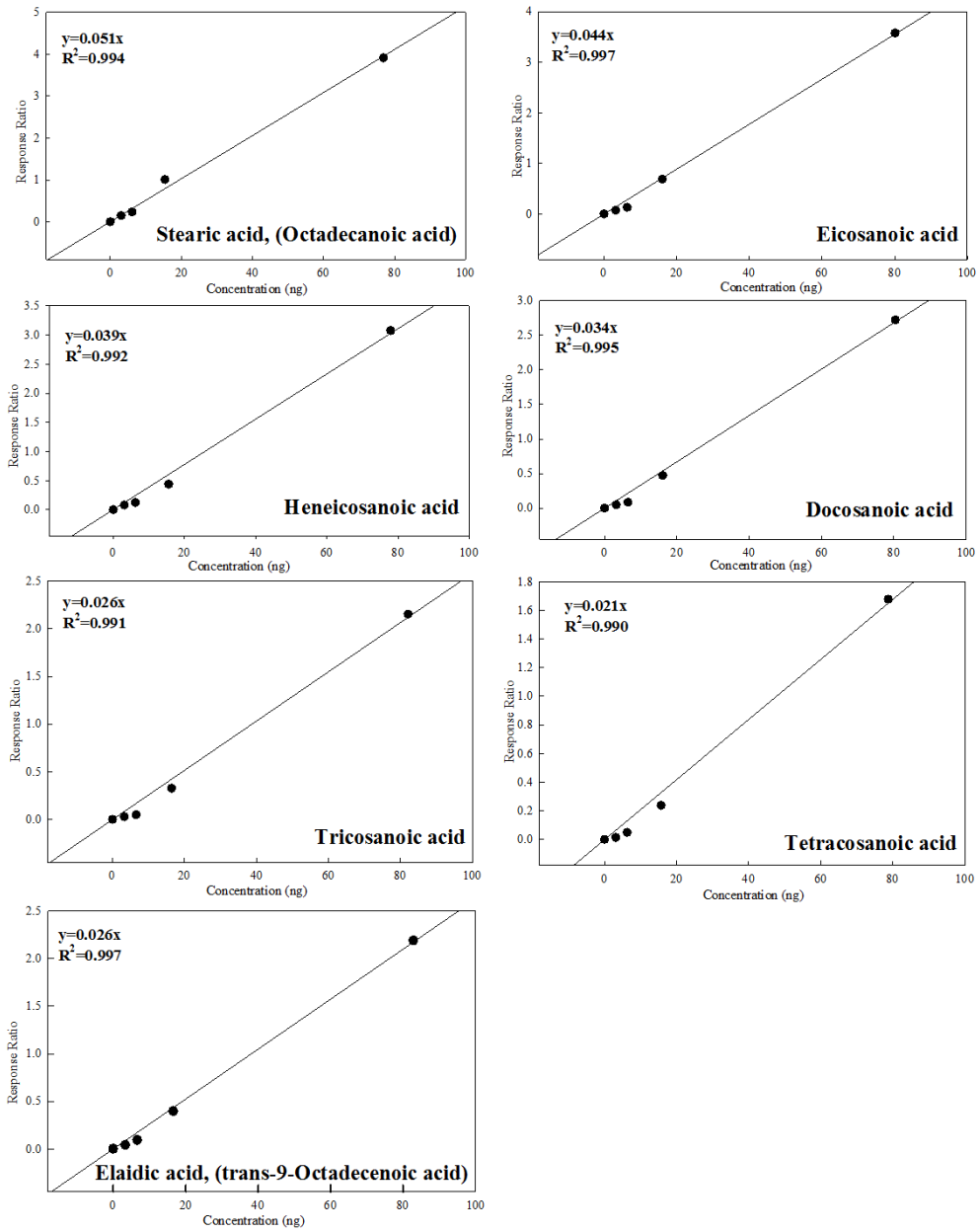

Fig. S3-9. (Continue)

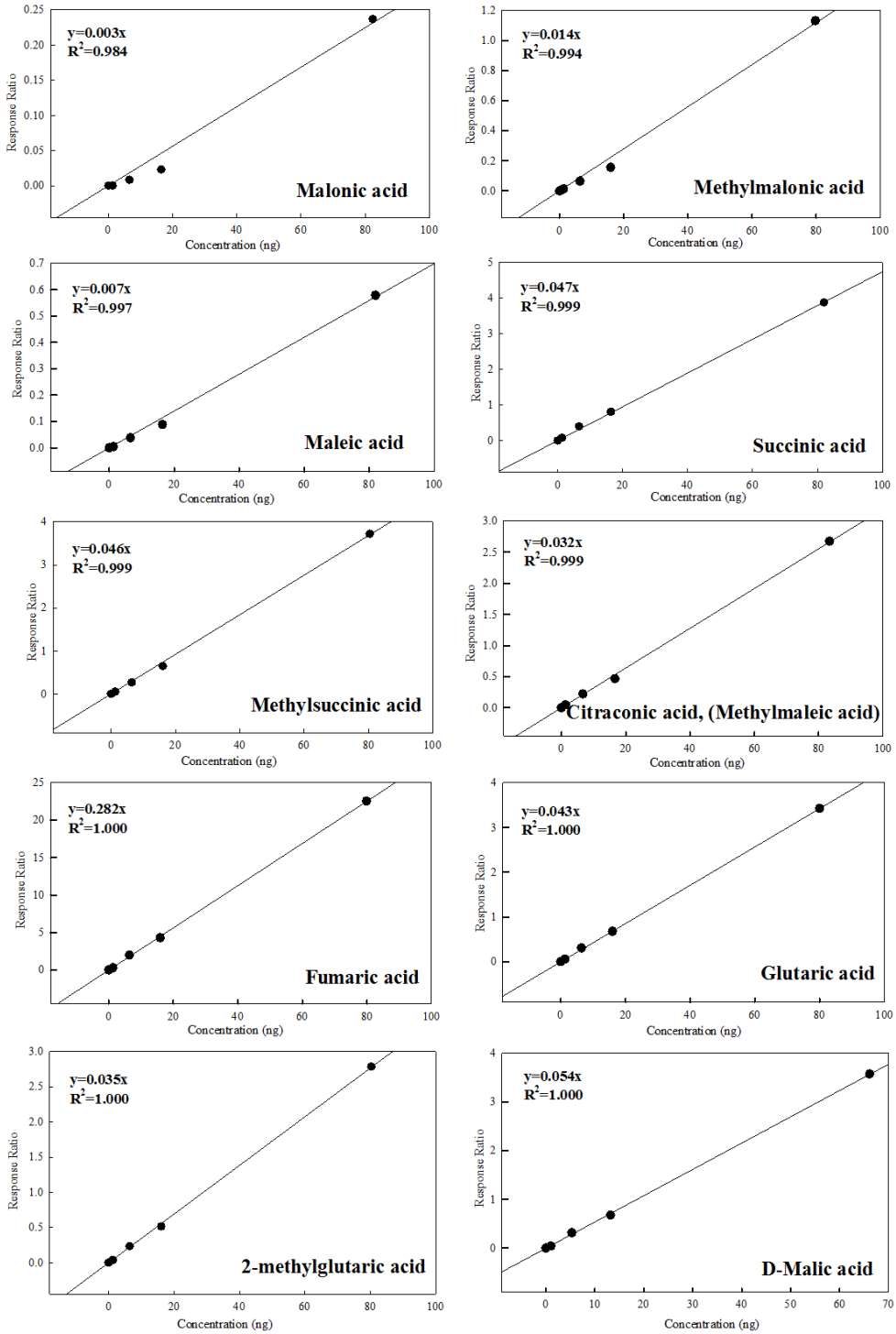

Fig. S3-10. Calibration curves of individual Dicarboxylic acids

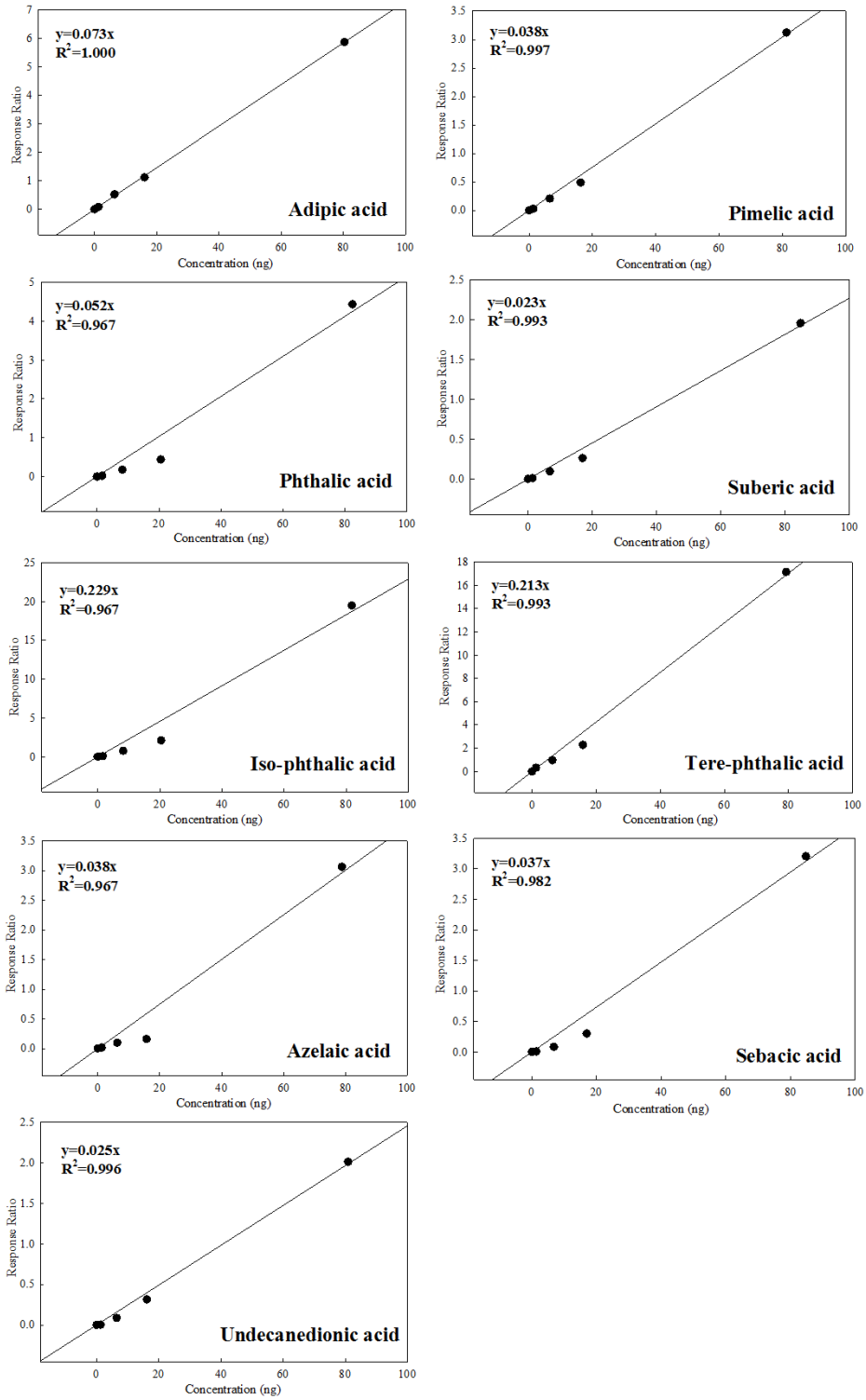

Fig. S3-10. (Continue)

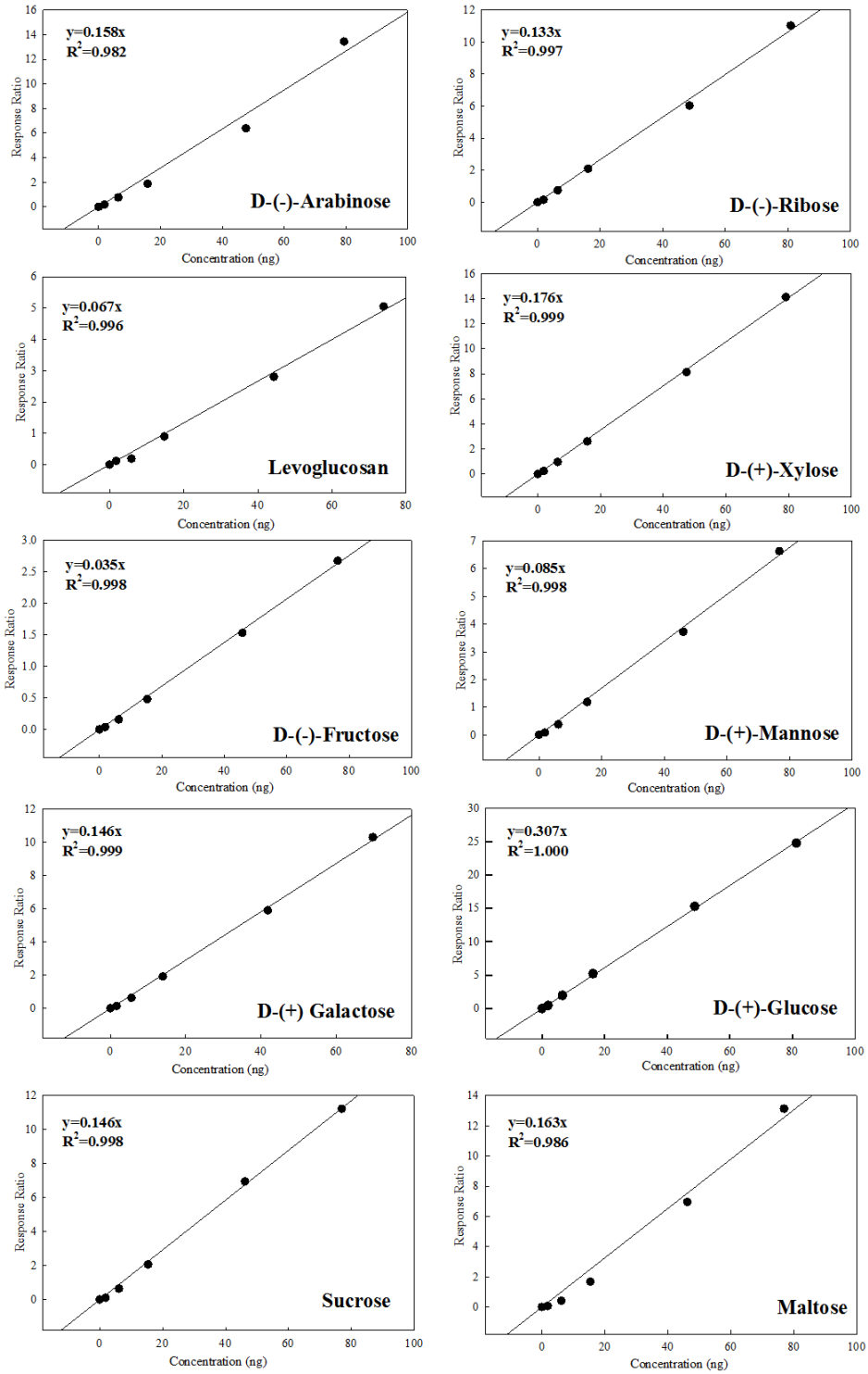

Fig. S3-11. Calibration curves of individual Sugars

Chapter 4. Conclusion and recommendations

4.1 Conclusions

The chemical composition and source identification of ambient $PM_{2.5}$ were determined over 6 months (May-October) in 2016. Daebu Island, which is the monitoring site in this study has regional characteristics of various mixed sources and thus the explicit analysis with analytical instruments and modeling techniques have been required for understanding the source contributions of $PM_{2.5}$.

For the chemical speciation of $PM_{2.5}$, both inorganic species and organic species were quantified. In chapter 2, inorganic speciation with 18 trace metal compounds (Cr, Mn, Cu, Fe, Ni, Pb, Cd, Mg, Al, V, Sr, Na, K, As, Se, Ca, Zn, and Co) and 4 ion species (Anions: Cl^-, NO_3^-, and SO_4^{2-}, Cation: NH_4^+) were defined whereas OC and EC concentration discovered the organic characteristics of airborne particles. The identification of the organic matters was more specified through TOC-V CPH total carbon analyzer and GC-MS, which enabled the measurement of WSOC, WIOC, SOC, and POC with total 77 of individual organic compounds.

The source identification with inorganic compounds has been more generally used due to less time-consuming steps and maintenance in analysis. However, for the clear understanding of potential sources, various organic markers with diagnostic ratio method should be required to obtain specific source contributions of ambient fine particulate matters. With the $PM_{2.5}$ speciation results, The PMF receptor modeling was performed in chapter 2 and total nine sources (Secondary Sulfate, Secondary Nitrate, Mobile, Coal Combustion, Non-ferrous Smelter, Industrial Activities, Soil,

and Aged Sea Salt) were defined with traditional markers. The PCA results from chapter 3 showed somewhat similar sources (Secondary Organic Aerosols (SOAs 1 and SOAs 2), Combustion related sources, Secondary inorganic factor, Biomass burning, and Industrial sources) and both of the receptor models indicated the secondary aerosol as the most abundant source of the sampling area though there was difference in the kind of model that has been applied as well as determined chemical species. Source apportionment with PMF provides daily source apportionment fractions that can be combined with meteorological data sets to perform hybrid models. The size of organic sample (n=38) used in chapter 3 was much smaller than the size (<100) required to perform PMF and thus there were limitations defining the origins of the source areas. For instance, SOC and WIOC were grouped in the same factor (SOAs 2) and that was estimated to be originated from anthropogenic emissions such as fossil fuel burnings. Therefore, it is recommended to provide information with possible source origins with hybrid receptor models in further studies.

Daebu Island showed diverse source characteristics as it was already expected from its geographical features. Anthropogenic sources from industrialized areas and mobile sources seemed to be transported from megacities near Daebu Island, but at the same time the sampling site showed features of a rural site with high contributions of plant wax as well as marine characteristics with aged sea salt sources. The sources from natural (plant wax or plants) seem to reflect the local characteristics of the sampling site whereas other sources, especially secondary sulfate and secondary nitrate appeared to come from relatively further regions even cross the country. Anthropogenic sources and natural sources sometimes seemed to react each other (ex. Ages sea salt). The average $PM_{2.5}$ mass concentration was

generally lower than that of megacities in Korea but the major factors consist of $PM_{2.5}$ sources seemed to be affected by human activities.

The work from this study is expected to help understanding of source characteristics of Daebu Island, Korea.

4.2 Recommendations

Based on the study results, several recommendations and opportunities to improve this study were suggested below. In chapter 3, Water-Insoluble Organic Carbon (WIOC) and Secondary Organic Carbon (SOC) were grouped in the factor 4. The water-insoluble characteristics of SOC is not general, but the association between two factors has been reported with the high contributions in anthropogenic VOCs. It is expected that the anthropogenic VOCs may originate from industrial emissions or mobile sources since Secondary Sulfate (29%) and Mobile (22%) factor determined by PMF contributed the large fraction of the total $PM_{2.5}$ contributions. For these reasons, for defining potential source regions of water-insoluble SOC around the sampling site, the PMF analysis with the factors from PCA should be analyzed for identifying regions with high probabilities. Other receptor models, such as Chemical Mass Balance (CMB) with proper source libraries can be performed to reduce the limitations as well as provide further explanations of source apportionment trends.

요약(국문초록)

수용모델을 통한 대부도 지역 대기 중 $PM_{2.5}$의 오염원 추정

김선혜

서울대학교 보건대학원

환경보건학과 대기환경전공

초미세먼지($PM_{2.5}$)의 화학적 특성은 대기의 기후 변화에 영향을 줄 뿐만 아니라, 인체의 건강영향에 막대한 영향을 줄 수 있다. 초미세먼지의 복잡한 화학적 특성은 입자가 생성된 각각의 다른 환경을 반영하고 있기 때문에, 화학적 구성 성분 파악을 통해 초미세먼지의 오염원을 추정할 수 있다. 수용모델은 초미세먼지의 화학적 성분 데이터를 가지고 오염원을 추정하는 방법 중의 하나로, 다양한 수용모델을 결합하여 비교 · 분석 하는 것은 신뢰성 있는 데이터 해석을 위해서 필요한 과정이며, EPA를 포함한 여러 문헌들에서 여러 모델을 병행하여 사용할 것을 권장하고 있다. 본 연구에서는 유기물 지표와 미량금속원소, 탄소성분, 이온성분을 분석하여 수용모델의 입력자료로 사용하였고, 양행렬인자분석법(Positive Matrix Factorization, PMF)과

주성분분석 (Principal Component Analysis, PCA)를 포함한 여러 수용모델의 결과 해석을 통해 대부도 지역의 오염원을 추정하고자 하였다.

양행렬인자분석법을 수행하기 위해 저유량 에어샘플러를 통해 총 83개의 필터에 샘플을 포집하였으며, 2016년 5월 21일부터 11월 1일까지를 시료채취기간으로 선정하였다. 초미세먼지의 미량금속원소, 탄소성분, 이온성분들은 각각 유도결합플라즈마 질량분석기(Inductively Coupled Plasma Mass Spectrometry, ICP-MS), OC/EC analyzer, 이온크로마토그래피(Ion Chromatography, IC)를 통해 분석되었다. 대상 기간 중 평균 질량 농도는 $26.2 \pm 14.5\ \mu g\ m^{-3}$으로, 월별 최고농도와 최저농도는 각각 5월($46.5 \pm 14.7\ \mu g\ m^{-3}$) 과 8월($18.6 \pm 8.1\ \mu g\ m^{-3}$)로 드러났다. 본 분석을 통해 9개의 오염원이 산출되었다. 2차 황산염(Secondary Sulfate, 29.0%), 자동차 배출 오염원(Mobile, 22.0%), 2차 질산염(Secondary Nitrate, 13.2%), 오일 연소 오염원(Oil combustion, 10.1%), 석탄 연소 오염원(Coal combustion, 9.4%), 해염입자(Aged sea salt, 7.9%), 토양 오염원(Soil, 5.6%), 비철 제련 공정 오염원(Non-ferrous smelter, 1.7%) 순서로 대부도 지역의 초미세먼지 유입에 기여하는 것으로 나타났다.

CPF (Conditional Probability Function) 모델 및 PSCF (Potential Source Contribution Function) 모델 분석 결과, 중국의 동쪽 해안지역으로부터 2차 에어로졸이 다량 기인하며, 다른 오염원들은 주로 중국의 산둥 반도 또는 우리나라의 산업 단지로부터 이동된 것임을 확인하였다.

고유량 에어샘플러를 사용하여 채취한 총 38개의 샘플을 유기성분 분석에 사용하였고, 유기 성분의 농도 기여도는 Dicarboxylic acids (67.86%), n-Alkanoic acids (22.63%), n-Alkanes (8.63%), Sugars (0.47%), PAHs (0.41%) 순서로 나타났다. 본 연구에서 분석되었던 PAHs diagnostic ratio 분석 결과, PAHs의 오염원은 주로 산업활동 등에서 배출되는 연소 오염원의 영향을 보였으며, n-Alkanes를 활용한 CPI 및 WNA% 값의 경우 그 수치가 주로 생물 기원 오염원의 영향을 나타내어 대부도 주변의 식물 등의 오염원이 n-Alkanes의 발생에 기여를 한 것으로 추정되었다.

유기성분 분석 결과는 앞서 분석하였던 미량금속원소, 탄소성분, 이온성분들과 함께 주성분분석(Principal Component Analysis, PCA)에 적용되었다. 주성분분석을 통해 도출된 6개의 인자들은 이차 유기 에어로졸 오염원(Secondary organic aerosols 1, 38.568%), 비 수용성 이차 유기 에어로졸 관련 오염원(Secondary organic aerosols 2, 10.191%), 이차 무기 에어로졸 오염원(Secondary inorganic carbon, 7.434%), 생물 연소(Biomass burning, 5.833%), 산업활동 관련 오염원(Industrial sources, 4.455%) 로 분류되었다. 이 중 비 수용성 이차 유기에어로졸 관련 오염원의 경우, 인위적 휘발성 유기화합물(anthropogenic volatile organic compounds)의 영향을 받은 것으로 사료되었다.

본 연구에서 분석한 수용모델 결과를 통해, 대부도 지역은 인위적 요인 및 자연적 요인이 $PM_{2.5}$의 기여도에 모두 영향을 미치는 것으로 드러났으며, 그 중에서도 초미세먼지의 대부분이 2차 에어로졸 및 연소

오염원으로부터 기인한다는 결과를 도출하였다. 2차 에어로졸의 경우 많은 양이 중국으로부터의 장거리 이동을 통해 대부도로 유입되는 반면, 연소 오염원 기인 입자들의 경우 북한, 중국, 우리나라의 산업 단지를 포함한 비교적 다양한 배출원의 영향을 받는 것으로 드러났다.

……

주요어: 초미세먼지($PM_{2.5}$), 오염원 추정(Source apportionment), 양행렬인자분석법(Positive Matrix Factorization, PMF), Conditional Probability Function (CPF), Weighted Potential Source Contribution Function (PSCF), Organic molecular markers, 주성분분석(Principal Component Analysis, PCA)

학 번: 2015-24104